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Environmental Science and Engineering, Inc. "Final Report: Development of Optimum Treatment System for Wastewater Lagoons Phase II - Solvent Extraction Laboratory Testing." Prepared for USATHMA, 85 pp. October 1984.

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SUPERFUND TREATABILITY CLEARINGHOUSE ABSTRACT

Treatment Process: Physical/Chemical - Chemical Extraction

Media: Soil/Lagoon Sediment

Document Reference: Environmental Science and Engineering, Inc. "Final Report: Development of Optimum Treatment System for Wastewater Lagoons Phase II - Solvent Extraction Laboratory Testing." Prepared for USATHMA, 85 pp. October 1984.

Document Type: Contractor/Vendor Treatability Study

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Site Name: Ft. Wingate, NM; Navajo, AZ; and Shreveport, LA
(NPL - Federal facility)

Location of Test: Gainesville, FL

BACKGROUND: The U.S. Army surveyed innovative treatment techniques for restoration of hazardous waste lagoons and selected solvent extraction as cost-effective restoration for further study. This treatability study focuses on treatment of organic (explosive) contaminated lagoon sediments which are the result of munitions production operations. Primary contaminants of concern included the following explosives: TNT, DNT, RDX and Tetryl. This was a laboratory study of solid extraction where the solvent is used in excess and the effectiveness of a single contact is limited by the ability to physically separate the liquid and soil fractions. The treatability goal is to reduce explosive contaminant level to 10 mg/kg.

OPERATIONAL INFORMATION: Sediments tested were obtained from Navajo Army Depot (AD), AZ (predominantly volcanic cinders); Ft. Wingate AD, NM (mostly clay); and Louisiana Army Ammunition Plant. Explosive content of sediments ranged from 0.1-99% and moisture content ranged from 23.8-42.8%. (Report provides characteristics information on sediments.) Acetone was selected as the leaching agent based on the solubility of contaminants, cost, and availability. Laboratory tests included: solubility, leaching efficiencies, and settling tests. Solubility tests evaluated water/acetone ratios to determine optimum operational range for individual contaminants and mixtures. Leaching tests evaluated effectiveness of countercurrent extraction to determine contact time required for equilibrium of explosives between leachate and the sediments. Multiple leaching tests were performed by shaking sediment with acetone/water mixture in 1-liter graduated cylinders for 30 minutes followed by solid-liquid separation. Settling tests were performed on two soils with significant solid content to determine settling rate to aid in design of waste water treatment unit.

Report provides a discussion of sampling and analysis methods and provides limited QA/QC information.

PERFORMANCE: Laboratory leachability studies indicated that wet, explosive-laddened sediments can be effectively decontaminated by leaching with an acetone/water mixture. In general, three to four contact stages of 30 minutes each were required to reduce the explosives level to less than 10 mg/kg. A fifth contact stage with a 50% efficiency would have been required to achieve the goal for the Louisiana sediment. Solubility tests demonstrated a non-linear solubility of explosives with acetone/water. Saturated solutions between 50 and 90% acetone form a two-phase liquid solution which should be avoided since this could hinder penetration of solvent through sediment. A conceptual treatment system design is provided based on results of tests. Calculated 4 stage removal efficiencies are shown in Table 1.

CONTAMINANTS:

Analytical data is provided in the treatability study report. The breakdown of the contaminants by treatability group is:

| <u>Treatability Group</u> | <u>CAS Number</u> | <u>Contaminants</u> |
|------------------------------------|-------------------|---------------------------|
| W06-Nitrated Aromatic Compounds | 118-96-7 | Trinitrotoluene (TNT) |
| | 99-35-4 | Trinitrobenzene (TNB) |
| | 121-82-4 | Hexahydro-1,3,5-trinitro- |
| | | 1,3,5-triazine (RDX) |

TABLE 1

INITIAL SEDIMENT EXPLOSIVES CONCENTRATION, FINAL SEDIMENT
EXPLOSIVES CONCENTRATION, AND CALCULATED 4-STAGE
REMOVAL EFFICIENCIES

| <u>Sediment</u> | <u>Initial Explosives Concentrations (mg/kg)</u> | <u>Final Explosives Concentrations (mg/kg)</u> | <u>4-Stage Removal Efficiency (%)</u> |
|-----------------|--|--|---|
| Ft. Wingate AD | 1,200 | 6.0 | 99.5 |
| Navajo AD | 19,000 | 7.0 | 99.96 |
| Louisiana | 420,000 | 17.0 | 99.996 |

NOTE: This is a partial listing of data. Refer to the document for more information.

**REPORT AMXTH-TE-CR-84302
FINAL REPORT**

**DEVELOPMENT OF OPTIMUM TREATMENT SYSTEM
FOR WASTEWATER LAGOONS**

PHASE II

SOLVENT EXTRACTION LABORATORY TESTING

**CONTRACT DAAK11-81-C-0076
TASK ORDER 6**

Prepared by:

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October 1984

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Prepared for:

**U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
ABERDEEN PROVING GROUND, MARYLAND**

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LIST OF ACRONYMS AND ABBREVIATIONS

| | |
|----------|---|
| AAP | army ammunition plant |
| AD | army depot |
| AMCCOM | U.S. Army Armament, Munitions, and Chemical Command |
| ASTM | American Society for Testing and Materials |
| CFR | Code of Federal Regulations |
| COR | Contracting Officers Representative |
| DNT | dinitrotoluene |
| EPA | U.S. Environmental Protection Agency |
| ESE | Environmental Science and Engineering, Inc. |
| Ft. | fort |
| GC | gas chromatography |
| gm | gram(s) |
| gm/cc | gram(s) per cubic centimeter |
| HMX | cyclotetramethylenetetranitramine |
| HPLC | high-pressure liquid chromatography |
| l | liter(s) |
| ln | logarithm |
| mg/kg | milligram(s) per kilogram |
| mg/l | milligram(s) per liter |
| ml | milliliter(s) |
| OECD | Organization for Economic Cooperation and Development |
| RCRA | Resource Conservation and Recovery Act |
| RDX | cyclotrimethylenetrinitramine |
| SARMS | Standard Analytical Reference Materials |
| TCD | thermal conductivity detection |
| TNB | trinitrobenzene |
| TNT | trinitrotoluene |
| TSS | total suspended solids |
| USATHAMA | U.S. Army Toxic and Hazardous Materials Agency |
| UV | ultraviolet |

1.0 INTRODUCTION

1.1 BACKGROUND

Lagoons at U.S. Army installations throughout the United States have been used for disposal of wastewater and sludge from a variety of industrial operations, including:

1. Primary explosives manufacture,
2. Secondary explosives manufacture,
3. Explosives washout,
4. Load and pack,
5. Detonator load,
6. Metal plating, and
7. Propellant manufacture.

The U.S. Army, concerned that many of the lagoons may present a potential for contamination of surface and ground waters, has established an aggressive program of lagoon decontamination. The sheer magnitude of the effort dictates the development of appropriate technologies that are effective and safe, and more economical than conventional excavation and disposal technologies.

A study of innovative treatment techniques for restoration of hazardous-waste lagoons was conducted by Environmental Science and Engineering, Inc. (ESE) for the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), the results of which are detailed in a 4-volume report, AMXTH-TE-83232, September 1983. The primary objective of the study was to identify and evaluate cost-effective restoration methods, implementable by the late 1980s, which would be not only economical and effective but also applicable to similar problems at a number of locations and easily transportable. Broad applicability of treatment is required because lagoons at different installations are of various sizes, depths, and configurations and contain various amounts of water and sediments with a diverse range of contaminants.

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| Waste | Decontamination | RDX |
| Lagoon | Treatment | Tetryl |
| Sediments | Explosives | Acetone extraction |
| Solvent extraction | TNT | Solubility |
| Leaching | DNT | Hazardous |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) | | |
| <p>A laboratory-scale study was conducted to test the technical feasibility of applying acetone extraction to decontamination of wet explosives-laden lagoon sediments. The experimental approach was to determine pure explosive compound solubilities in acetone/water mixtures, and finally to test the effectiveness and efficiency of acetone leaching on actual lagoon sediments.</p> <p>The materials used in the solubility experiments were pure 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), cyclotrimethylenetrinitramine (RDX), and tetryl. Lagoon sediments were obtained from Ft. Wingate Army Depot (AD),</p> | | |

To characterize the problem, existing lagoon data were compiled and reviewed. In addition, to provide more complete data, samples from two lagoons were collected and analyzed. Concurrently, potential waste treatment techniques were investigated. Lagoons were initially divided into classifications according to the industrial process which generated the waste.

Although the lagoons studied were the product of six major process types, from the point of view of treatment the lagoons could be effectively classified into two types based on major contaminants: organics and inorganics. Organics-laden lagoons contain primarily reactive organic residues that may possibly be converted into nonreactive compounds. Inorganics-laden lagoons contain heavy metal concentrations potentially above the Resource Conservation and Recovery Act (RCRA) extraction procedure (EP) toxicity limit, which cannot be treated to a nonhazardous form but can only be recovered or isolated from the environment.

For inorganic wastes, current practice is disposal in a secure landfill. In many cases long-distance hauling is necessary. An economical alternative would appear to be chemical fixation followed by onsite landfilling or disposal in a sanitary landfill. Since fixation technology is being studied by USATHAMA under a separate contract, no techniques for restoring lagoons containing inorganic hazardous wastes were recommended for further study.

The current state-of-the-art technology for hazardous organic materials is incineration; therefore, incineration serves as a baseline for evaluating treatment alternatives. The ESE report identified two promising alternative treatment methods: aqueous thermal decomposition and solvent extraction. Aqueous thermal decomposition involves the heating of sediment in an aqueous slurry under pressure to temperatures of between 200 and 300°C. The solvent extraction technique utilizes an

organic solvent to leach the hazardous components from sediment, thereby separating and concentrating the hazardous portion.

Subsequent to the September 1983 report, ESE initiated a laboratory program to test the feasibility of aqueous thermal decomposition and solvent extraction. The results of the aqueous thermal decomposition study will be submitted in a separate report, as will a discussion of the engineering design of each technology to treat lagoon sediments at three U.S. Army ammunition plant (AAP) facilities. This report presents the results of the solvent extraction laboratory study.

"Solvent extraction" is a technique of selectively separating and removing one or more specific constituents from a mixture by use of a solvent. There are two major categories of solvent extraction: liquid extraction and solid extraction. The category applicable to this study is solid extraction.

While liquid extraction and solid extraction have a common basis, a fundamental difference is that liquid extraction is equilibrium-limited while solid extraction is not. In other words, in liquid extraction the amount of solute that can be separated from a mixture by a single contact is limited by equilibrium relationships among liquids in the mixture. In solid extraction processes, excess solvent is generally used, and the effectiveness of a single contact is limited by the ability to physically separate the liquid and solid fractions.

Solid extraction is often referred to as "leaching." When the soluble material is largely on the surface of the insoluble solid and is merely washed off by the solvent, the operation is sometimes called "elution" or "elutriation." The term leaching is more common and often used interchangeably with extraction.

1.2 REGULATORY CONSIDERATIONS

The majority of U.S. Army lagoons containing organics-contaminated sediments are the result of munitions production operations. These lagoons pose a particular problem under RCRA of 1976, which directed the U.S. Environmental Protection Agency (EPA) to promulgate regulations for the management of hazardous wastes. In the Title 40 Code of Federal Regulations (CFR), Part 261, Subpart D, wastewater treatment sludges from the manufacturing and processing of explosives and pink/red water from trinitrotoluene (TNT) operations are listed as "hazardous wastes from specific sources."

Classification as hazardous wastes under Subpart D is independent of the nature of the sludge and is not affected by any treatment performed on the sludge. However, Title 40 CFR Part 260.22 does provide for "delisting" of a particular waste if it can be shown that the waste does not exhibit the characteristic for which it is listed (i.e., reactivity). But because protocols for reactivity testing have not been established in the regulation, there are no criteria for proving the nonreactive nature of an explosives-processing sludge or the residues from its treatment.

It appears, then, that landfilling of any sludge resulting from the manufacture of explosives or the residue of its treatment is precluded, no matter how inert and innocuous the material may be. However, EPA has in some cases agreed to accept chemical evidence in the place of reactivity testing to prove that no reactive species are present. In addition, the U.S. Army is actively working to establish reactivity tests acceptable to EPA for delisting purposes. Thus, it is reasonable to expect that in the near future landfilling of sludges from explosives manufacturing and loading operations will be permitted if it can be shown that the reactive components have been effectively removed or destroyed. For purposes of this study, removal to less than 10 milligrams per kilogram (mg/kg) is assumed to be effective enough for reactivity delisting.

1.3 OBJECTIVES

The objective of this laboratory program was to test the technical feasibility of using solvent extraction techniques to separate organic explosives from inert material in lagoon sediments. Experiments were included to determine operating parameters for design of pilot- and full-scale systems.

Several solvents, including water, benzene, toluene, acetonitrile, and acetone, were considered for use in the laboratory study. Acetone was selected as the best solvent for leaching explosives-laden sediments because all explosives of interest are quite soluble in it, and also because acetone is relatively inexpensive, nontoxic, and readily available in bulk. It is miscible with water in all proportions; therefore, interfacial effects do not hinder penetration of solvent in wet sediments.

The solubilities of individual explosives in pure acetone and in pure water are available in the literature; however, the solubilities in acetone-water mixtures are not. Because many explosives-contaminated lagoons are wet, the determination of solubilities of explosives as a function of the acetone-water ratio in the solvent is necessary for design of a treatment system. It is also important to know the solubility of mixtures of explosives in various acetone/water solutions.

To evaluate acetone-water mixtures, a 3-step experimental approach was used to determine:

1. Individual solubilities of explosives as a function of acetone-water ratio in the solvent,
2. The effect of mixing explosives on overall solubilities, and
3. The effectiveness of solvent extraction on real sediments.

2.0 BASIC PRINCIPLES

In this section some basic principles are discussed. The purpose of this section is to present concepts necessary to understand the experimental results. The discussions here are brief. More detailed information can be obtained from the references cited in this section.

2.1 PHASE EQUILIBRIUM

The TNT/acetone/water, dinitrotoluene (DNT)/acetone/water, and mixed explosives/acetone/water systems unexpectedly formed two liquid phases in equilibrium with solid solute. This is probably because of the hydrophobic nature of TNT and DNT evidenced by their low solubility in water.

The thermodynamic criteria for phase separation and stability are expressed in terms of Gibbs free energy. According to Smith and Van Ness (1975), "The equilibrium state of a closed system is that state for which the total Gibbs free energy is a minimum with respect to all possible changes at a given temperature and pressure." Thus, a 2-phase system is formed if the total Gibbs free energy of the system is lower than that of a 1-phase system. In a 2-phase system, the individual chemical components will distribute at equilibrium between the phases such that their chemical potential is the same in each phase.

It is customary to present ternary phase equilibrium data on triangular coordinates. Such diagrams contain a wealth of information. Consider, for example, Figure 2-1, the ternary phase diagram developed in this study for TNT/acetone/water system at 25°C. The experimental results are discussed in the next section, but the diagram will be used here to show the use of triangular coordinates.

The use of triangular phase diagrams, discussed in detail by Treybal (1980), is based on the fact that the sum of the perpendicular distances to the sides from any point within an equilateral triangle is equal to

the altitude of the triangle. Thus, if each apex of the triangle represents one of the pure components, the perpendicular distance to the side opposite that apex, divided by the altitude of the triangle, is the fraction of that component in the mixture. The sum of the three fractions for any point within the triangle is equal to one.

In Figure 2-1, pure TNT is represented by the top apex, pure water by the left apex, and pure acetone by the right apex. Points along the base of the triangle represent acetone/water mixtures with no TNT. The left and right sides represent water/TNT and acetone/TNT binary mixtures, respectively. The perpendiculars from each apex to the opposite side are marked with 100 gradations representing weight-percent values. The point marked "B," where four curves meet, is 4 units from the base and thus represents 4-percent TNT. Point B is 51 units from the left side and 45 units from the right. Therefore, the composition at Point B is 4-percent TNT, 51-percent acetone, and 45-percent water.

Using Figure 2-1, the phase behavior of any mixture of TNT, acetone, and water at 25°C can be predicted. Mixtures with compositions that fall in the 3-phase region bounded by Points B, C, and E will consist of two liquids and a solid. The solid will be pure TNT corresponding to Point E. The liquid phases will have compositions corresponding to Points B and C. The relative amounts of each phase will change depending on the proportion of each component in the starting mixture, but the composition of the three phases will always correspond to Points E, B, and C if the overall composition of the system falls in the 3-phase region.

The lever rule can be used to calculate the relative proportions of the phases. For example, a starting composition at Point F will have three phases at equilibrium. Applying the lever rule, a tie line from Point E through Point F intersects Line BC at Point G. The weight of solid TNT at equilibrium will be proportional to the length of Line FG divided by

the length of Line EG. The weight of the two liquid phases together will be proportional to Line EF divided by Line EG.

The relative amounts of the two liquid phases formed by the mixture at Point F can be determined by applying the lever rule to Line BGC. The weight of the water-rich phase corresponding to the composition at Point B is proportional to Line GC divided by Line BC, and the weight of the TNT-rich phase is proportional to Line BG divided by Line BC.

There are three separate regions of 2-phase equilibria in the TNT/acetone/water system. Two regions of liquid-solid equilibria are bounded by Points A, B, and E and by Points C, D, and E. In these two regions, solid TNT is in equilibrium with saturated liquid. Tie lines extend from the TNT apex to the saturation curve as in the 3-phase region.

In the 2-phase liquid-liquid region, a water-rich liquid is in equilibrium with a TNT-rich liquid neither of which is saturated with TNT. In this region it is possible to define tie lines connecting the equilibrium phase compositions similar to line BGC for the saturated solutions. The ties usually run in the same general direction as line BGC but are not necessarily parallel and must be determined experimentally. It is obvious that the tie lines grow shorter as they approach the acetone apex and the compositions of the two phases approach each other. The final point where the phase compositions are equal is the "plait point." Mixtures richer in acetone than at the plait point will form a single liquid phase.

2.2 SETTLING TESTS

In order to design sludge thickeners and clarifiers, the settling velocity of the solid particles must be determined. From the settling velocity a clear liquid overflow rate can be determined and the vessel diameter calculated.

Dilute suspensions of solids generally exhibit three settling regimes. Initially in the "free settling" regime the individual particles are separated by fluid and do not interact with one another. As the slurry settles and becomes more concentrated, particle-particle interactions become significant and the settling rate slows. This is called the "hindered settling" regime. Finally, in the "compression" regime, sludge settles very slowly as particles pack together.

2.3 LEACHING STAGE EFFICIENCY

In a leaching operation where the solid is leached with more than enough solvent and given sufficient time to dissolve all the soluble portion, complete removal of solute could be accomplished in one stage if a perfect separation of solution from the inert solid were possible. In practice, two phenomena combine to yield stage efficiencies of less than 100 percent: adsorption and entrainment.

Adsorption is the ability of certain solids to preferentially concentrate specific substances on their surfaces. Adsorption can be either a physical or chemical phenomenon, depending on the nature of the materials involved. It can contribute to the carryover of solute with solids in leaching operations. Because adsorption is an equilibrium process, the amount of adsorbed material depends on the concentration of solute in solution. Depending on the equilibrium relationship, effective removal of adsorbed solute could require several contact stages.

Entrainment is caused by the imperfect mechanical separation of solids and solution. Because liquid-solid separations are not perfectly efficient, some liquid and dissolved solute are retained in the solids. Entrainment effects can be found by the calculation of a material balance around the contact stage. The weight of entrained solute can be calculated from the amount of moisture in the solids leaving the stage and the concentration of solute in the liquid leaving that stage.

The time required to reach equilibrium depends on the nature of the leached material. If the solute is mainly on the surface of the particles and is merely washed off, the approach to equilibrium is rapid. If the solute is confined in the internal structure of individual particles, it must diffuse to the surface of the particle before it can enter the bulk solution. These mass transfer limited leaching processes are much slower in approach to steady state. Stage efficiencies will be reduced if contact time is not long enough to reach equilibrium.

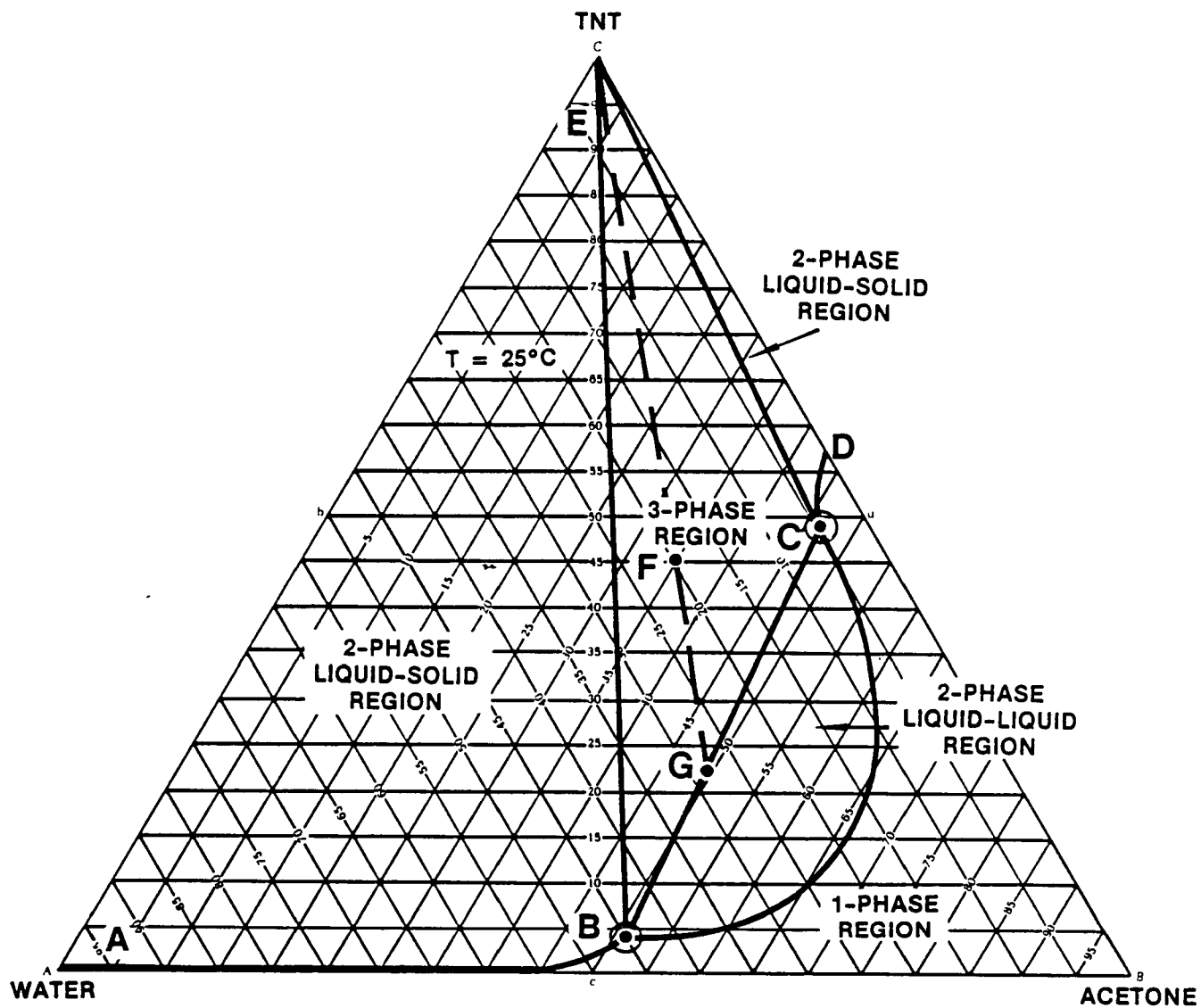


Figure 2-1
TNT/ACETONE/WATER PHASE DIAGRAM,
WEIGHT-FRACTION BASIS

SOURCE: ESE, 1984.

USATHAMA

3.0 EXPERIMENTAL PROCEDURES

This section discusses the experimental methodology and bases for conducting solvent extraction experiments, the procedures used in conducting these experiments, and the materials used.

3.1 EXPERIMENTAL MATERIALS

3.1.1 Explosives

The solubilities of 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), cyclotrimethylenetrinitramine (RDX), and tetryl, individually and in combination, were determined over a range of water/acetone mixtures. 1,3,5-trinitrobenzene (TNB) was initially scheduled to be included for solubility testing; however, sufficient quantities of TNB were not available.

TNT, with 10-percent water added, was purchased from Eastman Kodak Company, Rochester, New York. DNT was purchased from Aldrich Chemical Company, Milwaukee, Wisconsin, and ICN Pharmaceuticals, Cleveland, Ohio. The DNT and TNT were recrystallized from 95-percent ethanol and dried in a convection oven.

RDX, wetted with isopropyl alcohol, was received by ESE from the U.S. Army Armament, Munitions, and Chemical Command (AMCCOM), Rock Island, Illinois. The RDX was recrystallized from acetone and dried in a convection oven. The resulting crystals were analyzed chromatographically by comparison with USATHAMA Standard Analytical Reference Materials (SARMs) and were found to contain 99.1-percent by weight RDX and 0.7-percent cyclotetramethylenetetranitramine (HMX).

Tetryl was received from AMCCOM, Rock Island, Illinois. The tetryl, as obtained, assayed at greater than 99-percent purity by comparison with USATHAMA SARMs and was used without further purification.

3.1.2 Solvents

High-purity water and distilled-in-glass acetone were purchased from Burdick and Jackson Laboratories, Inc., Muskegon, Michigan, and used without further purification.

3.1.3 Sediments

Explosives-contaminated lagoon sediments were required to complete the experimental program. An ESE representative and the USATHAMA Contracting Officers Representative (COR) obtained three separate sediment samples from Ft. Wingate Army Depot (AD) in Gallup, New Mexico; Navajo AD in Flagstaff, Arizona; and Louisiana Army Ammunition Plant (AAP) in Shreveport, Louisiana.

At each site, sediment samples were removed from the lagoon with a plastic scoop and placed in 2-quart glass jars with Teflon® lid liners. No field preservation was necessary. Upon arrival at ESE's laboratories, each sediment sample was homogenized separately and stored at 4°C in the original glass jar.

The physical appearance of the sediments varied. The Navajo AD sediment was predominately volcanic cinders, the Ft. Wingate AD material was mostly clay, and the Louisiana AAP sediment was visibly contaminated with yellow crystals.

3.2 EXPERIMENTAL METHODS

3.2.1 Characterization of Sediments

Each of the three sediments was analyzed for explosives, metals, and other standard parameters. The results are presented in Table 3-1. The explosives and moisture data are particularly pertinent to the solvent extraction testing. The metals, anions, pH, and acidity/alkalinity data, although shown in Table 3-1, were obtained primarily for consideration in catalysis of aqueous thermal decomposition of explosives wastes studied separately under this task order. The data show that the moisture

Table 3-1. Characterization Data for Sediments Used in Solvent Extraction and Aqueous Thermal Decomposition Testing

| Parameter | Navajo AD | Ft. Wingate AD | Louisiana AAP |
|---|--------------|-------------------|------------------|
| pH (Standard Units) | 6.7 | 4.6 | 7.2 |
| NO ₂ + NO ₃ (mg/kg-dry) | 2 | 0.2 | 21 |
| Sulfate (mg/kg-dry) | <25 | <25 | <25 |
| Total Organic Carbon (g/kg-dry) | 21 | 5.8 | 26.0 |
| Phenols (ug/kg-dry) | 1,500 | 180 | NA |
| Nitrogen, TKN (mg/kg-dry) | 990 | 1,000 | 51,000 |
| Alkalinity (mg/kg-total) | 9.4 | 59 | 7.8 |
| Moisture (%) | 24.0 | 28.0 | 43.0 |
| Chloride (mg/kg-dry) | <250 | <250 | <250 |
| Acidity (mg/kg-total) | 2.10 | 1,600 | 4.80 |
| Total Phosphorus (mg/kg-dry) | 610 | 27,000 | 82.0 |
| Chromium (mg/kg-dry) | 39 | 24.0 | 5.6 |
| Lead (mg/kg-dry) | 120 | 170 | <25.0 |
| Aluminum (mg/kg-dry) | 7,800 | 8,300 | 290 |
| Antimony (mg/kg-dry) | <22 | <23 | <30 |
| Magnesium (mg/kg-dry) | 10,000 | 2,800 | 64 |
| Sodium (mg/kg-dry) | 1,300 | 8,800 | 38 |
| Copper (mg/kg-dry) | 21 | 23 | 33 |
| Zinc (mg/kg-dry) | 270 | 120 | 72 |
| Iron (mg/kg-dry) | 14,000 | 13,000 | 1,100 |
| Barium (mg/kg-dry) | 50 | 230 | 25 |
| Calcium (mg/kg-dry) | 7,200 | 18,000 | 510 |
| RDX (mg/kg-dry) | 25 | 1.9 | 85,000 |
| HMX (mg/kg-dry) | 34.0 | <0.9 | 11,000 |
| 2,4,6-TNT (mg/kg-dry) | 20,000 | 730 | 870,000 |
| 2,4-DNT (mg/kg-dry) | <500 | 5.6 | 180 |
| 3,5-DNB (mg/kg-dry) | <250 | 1.8 | <50 |
| 1,3,5-TNB (mg/kg-dry) | <330 | 3.9 | 84.0 |
| Tetryl (mg/kg-dry) | <250 | <1.4 | 26,000 |

Source: ESE, 1984.

content varied from 23.8 percent to 42.8 percent, and explosives concentration varied from less than 0.1 percent to almost 99 percent in the three sediments. Thus, it appears that a good cross section of sediment types was available for the experimental program.

The explosives were analyzed according to the documented method, using acetone extraction with high-performance liquid chromatography/ultra-violet (HPLC/UV) detection (see Appendix A). TNT was the major explosive of interest, and because of the high TNT levels in the sediments, substantial dilution of the extracts was required to bring the TNT into the range of the analytical standard curve. Consequently, the detection limit of other explosive components varied for the different sediments. The moisture levels were determined gravimetrically as specified in Appendix A.

3.2.2 Solubility Experiments

3.2.2.1 Individual Explosives

The solubilities of TNT, DNT, RDX, and tetryl were determined in water/acetone mixtures, using a modified version of the Organization for Economic Cooperation and Development (OECD) 1978 water-solubility protocol.

The size of each sample prepared was selected to yield a volume large enough for easy sampling without using excessive amounts of materials. If a particular fraction was expected to form two liquid phases (as discussed in Section 4.0), a larger sample was prepared so that each phase could be sampled and analyzed. This was particularly important for samples in which one phase was disproportionately larger than the other.

The OECD protocol requires periodic reanalysis of a sample fraction to determine whether equilibrium has been established. Agreement within 15 percent between successive analyses is considered proof of equilibrium. This was not possible with the explosives/acetone/water

systems in this study. In order to measure the volumes of the two liquid phases, the entire sample must be transferred from the vial to a graduated cylinder. During the transfer, evaporation of acetone was unavoidable, and if the sample was transferred several times, its composition would change. In order to circumvent this problem, quadruplicate samples were prepared. Duplicate sets of samples were analyzed at least 24 hours apart, and agreement within 15 percent was taken as proof of equilibrium.

Seven acetone/water mixtures were prepared, with 0, 33, 50, 67, 80, 90, and 100 weight-percent acetone. The acetone/water ratios were chosen based on preliminary experiments which indicated more rapid solubility changes and two-liquid-phase behavior in mixtures with greater than 50 percent acetone. The acetone/water mixtures containing an excess of the solid explosive (using the literature values of solubility in acetone and in water as a guideline) were placed in separate amber vials and sealed with Teflon®-lined septum caps. The solubility test schemes for the four explosives are shown in Table 3-2.

The test samples were incubated at 35°C for 24 hours. The temperature of the incubator was then adjusted and maintained at 25°C, and the samples were equilibrated for 48 hours. At the end of this period, the liquid was removed, and the liquid-phase volumes were measured in a graduated cylinder or test tube. A portion of each liquid phase was removed and filtered through a 0.45-micron Nylon 66 filter (Rainin Instrument Company, Woburn, Massachusetts) using a syringe filter. The filtrate was analyzed using HPLC/UV detection for explosives and using gas chromatography/thermal conductivity detection (GC/TCD) for water and acetone.

3.2.2.2 Mixed Explosives

The mixed-explosives solubility test was performed in the same manner as the individual solubility tests. An excess of TNT, DNT, RDX, and tetryl

Table 3-2. Individual Explosives Solubility Test Scheme

| Weight- Percent Acetone in Solvent | Solvent (ml) | TNT (gm) | DNT | | RDX | | Tetryl | |
|---|-----------------|-------------|-----|-----|-----|-----|--------|-----|
| | | | ml | gm | ml | gm | ml | gm |
| 0 | 4 | 0.3 | 4 | 0.3 | 5 | 0.3 | 4 | 0.3 |
| 33 | 50 | 4 | 25 | 2 | 25 | 1 | 25 | 3 |
| 50 | 50 | 6 | 25 | 3 | 25 | 2 | 25 | 5 |
| 67 | 50 | 14 | 25 | 11 | 25 | 3 | 25 | 9 |
| 80 | 4 | 5 | 4 | 5 | 5 | 2 | 10 | 7 |
| 90 | 4 | 5 | 4 | 5 | 5 | 2 | 10 | 8 |
| 100 | 4 | 6 | 4 | 6 | 5 | 2.5 | 4 | 6 |

Note: ml = milliliters.
gm = grams.

Source: ESE, 1984.

Table 3-3. Mixed Explosives Solubility Test Scheme

| Weight- Percent Acetone in Solvent | Solvent (ml) | TNT (gm) | DNT (gm) | RDX (gm) | Tetryl (gm) |
|---|-----------------|-------------|-------------|-------------|----------------|
| 0 | 4 | 0.1 | 0.1 | 0.1 | 0.1 |
| 33 | 4 | 4.1 | 4.1 | 0.8 | 0.6 |
| 50 | 4 | 4.1 | 4.1 | 0.9 | 0.6 |
| 67 | 10 | 8.4 | 8.3 | 1.1 | 1.7 |
| 80 | 1 | 5.0 | 5.0 | 2.5 | 2.5 |
| 90 | 4 | 7.5 | 7.0 | 1.1 | 2.5 |
| 100 | 1 | 5.0 | 5.0 | 2.5 | 2.5 |

Source: ESE, 1984.

was added to each sample. Because the combined explosives had enhanced solubilities over individual explosive solubilities, several additions of explosives were necessary to achieve saturation. These experiments were not duplicated because of the large quantities of explosives required. The final test scheme is shown in Table 3-3.

3.2.3 Leach Rate Experiments

Leach rate experiments were conducted on the three sediments to determine the contact time required for equilibration of the explosives between the leachate and the sediment. Ratios of acetone to sediment were selected so that the water present in the sediment would dilute the acetone to 90 percent by weight. The results of the solubility experiments were used to make sure the solubility limits were not exceeded. The levels of explosives naturally occurring in the sediments were less than one-half the levels required for saturation of the 90-percent acetone leachate. Because of the high percent of moisture and high levels of explosives in the Louisiana AAP sediment, the sediment was diluted 1:1 with masonry sand. The test scheme for the leach rate tests is presented in Table 3-4.

Table 3-4. Leach Rate Test Scheme

| | Ft. Wingate AD | Navajo AD | Louisiana AAP |
|-------------------|-------------------|--------------|------------------|
| Acetone (ml) | 285 | 285 | 285 |
| Sediment (gm)* | 90 | 105 | 61.3 |
| Masonry Sand (gm) | -- | -- | 61.3 |

*As received.

Source: ESE, 1984.

respectively. The stream designators in the squares at the bottom represent the final simulated streams which are sampled and analyzed.

In Stage 1A, fresh sediment and fresh acetone are contacted and separated. The liquid portion is discarded, and the solids are carried over to Stage 2A and contacted with fresh solvent. The liquid from Stage 2A is contacted with fresh sediment to form Stage 1B. The solids from Stage 2A are contacted with fresh solvent to make Stage 3A. At this point, Stage 1B and Stage 3A have been prepared. In Step 4, the proper liquid and solid portions are discarded or carried on for Stage 2B and Stage 4A.

This process is repeated until a liquid stream and a solid stream that have contacted four stages are obtained, which occurs in Step 7 for the liquid stream and Step 8 for the solid stream. In the scheme shown in Figure 3-1, the procedure is taken through Steps 9 and 10 to assure steady-state conditions. "

The countercurrent leaching experiments were conducted in 1-liter graduated cylinders with ground-glass stoppers. Each contact stage was manually shaken vigorously for 30 minutes. Solid-liquid separation was accomplished by vacuum filtering through Whatman No. 4 filter paper.

The quantity of sediment used in the experiment was selected to yield a final solid sample large enough to analyze, while keeping solvent usage and waste generation low. The quantity of acetone was selected to yield a final liquid stream of approximately 10-percent water in the solvent and also yield a final explosives concentration below saturation. The 10-percent water criterion was selected based upon the solubility experiments. The quantities used are shown in Table 3-5.

Table 3-5. Countercurrent Extraction Feed Scheme

| Sediment Source | Sediment Quantity (gm) | Acetone Quantity (ml) |
|-----------------|------------------------|-----------------------|
| Ft. Wingate AD | 140 | 450 |
| Navajo AD | 140 | 385 |
| Louisiana AAP | 210 | 675 |

Source: ESE, 1984.

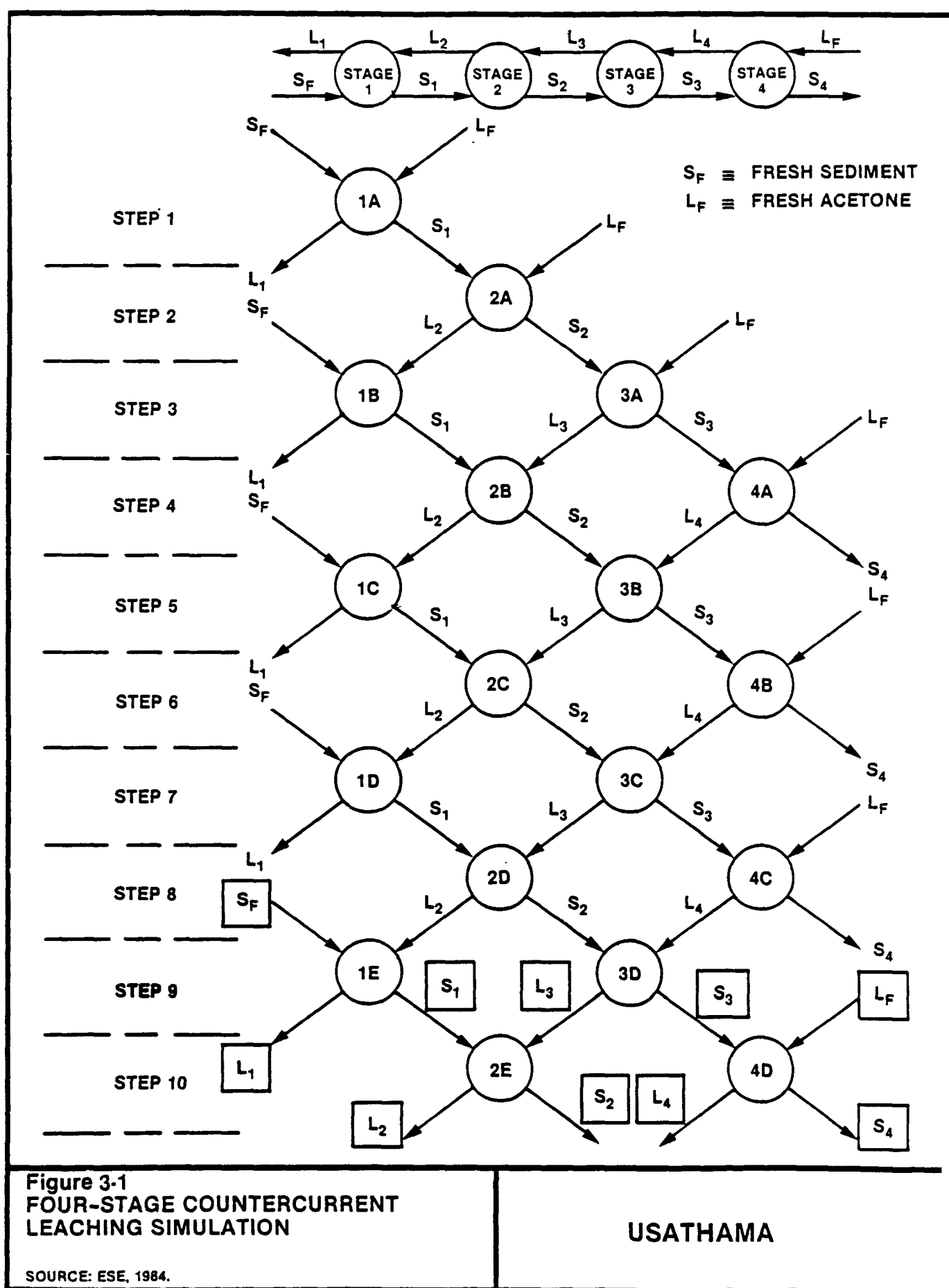
The final liquid stream and intermediate streams were analyzed using HPLC/UV detection for explosives content and GC/TCD for acetone and water content. The solid samples were extracted using the method detailed in Appendix A and analyzed for explosives content using HPLC/UV detection.

3.2.5 Settling Tests

Settling tests were performed with Ft. Wingate AD and Navajo AD sediments. The tests were performed in the 1-liter graduated cylinders used for the countercurrent leaching simulation using acetone/water ratios corresponding to Stage 1. No test was performed with the Louisiana AAP sediment because of its low concentration (2 percent) of inert solids.

The sediment/acetone/water mixtures were initially shaken to suspend the inert particles. After shaking, the height of the sludge/clear liquid interface was measured at 15-second intervals. As the settling rate decreased, sludge height measurements were taken at longer intervals. The experiment was terminated after 60 minutes as the settling rate slowed in the compression regime.

At the end of the settling tests, the supernatant was filtered through tared Whatman No. 42 filter paper. The paper was air dried and weighed to determine the suspended solids content of the supernatant.



4.0 EXPERIMENTAL RESULTS

4.1 INDIVIDUAL EXPLOSIVE SOLUBILITIES

The results of the ternary system solubilities of individual explosives in acetone/water mixtures are presented in this section. The ternary systems investigated were:

- o TNT/acetone/water,
- o DNT/acetone/water,
- o RDX/acetone/water, and
- o Tetryl/acetone/water.

4.1.1 TNT Solubility

When the TNT/acetone/water solutions were prepared, the 67-, 80-, and 90-percent acetone samples split into a water-rich top phase and a TNT-rich bottom phase.

The analytical results of the TNT/acetone/water experiments are shown in Table 4-1. Compositions of the water-rich fractions, including the 1-phase, 0-, 33-, and 50-percent acetone samples, are listed in the left-side columns of the table. Data listed in the right-side columns are for the TNT-rich fractions, including the 1-phase 100-percent acetone sample.

Figure 2-1 was generated from the analytical solubility data, augmented with physical titration experiments and assumptions based on knowledge of similar ternary systems. Curve ABCD, based on the solubility experiment data, is the saturation curve for TNT in acetone/water.

Curve BC, between the 2-phase liquid-liquid region and the 1-phase region, was defined using two types of titration experiments. In the first set of experiments, binary mixtures of acetone and water (represented by Points A, B, C, D, and E in Figure 4-1) were titrated with pure TNT until the solution became cloudy, indicating the onset of 2-phase behavior. Incremental addition of TNT drives the concentration

Table 4-1. TNT Solubility in Acetone/Water

| Initial Weight- Percent Acetone | Water-Rich Fractions | | | | TNT-Rich Fractions | | | |
|--|----------------------|-----------------|---------|--------|--------------------|-----------------|---------|------|
| | Volume Percent | Weight Fraction | | | Volume Percent | Weight Fraction | | |
| | | Water | Acetone | TNT | | Water | Acetone | TNT |
| 0 | 100 | 0.9999 | 0 | 0.0001 | 0 | — | — | — |
| 33 | 100 | 0.68 | 0.32 | 0.002 | 0 | — | — | — |
| 50 | 100 | 0.51 | 0.47 | 0.02 | 0 | — | — | — |
| 67 | 61.7 | 0.43 | 0.53 | 0.04 | 38.3 | 0.05 | 0.50 | 0.45 |
| 80 | 13.3 | 0.45 | 0.51 | 0.04 | 86.7 | 0.05 | 0.43 | 0.52 |
| 90 | 2.4 | * | * | * | 97.6 | 0.05 | 0.45 | 0.50 |
| 100 | 0 | — | — | — | 100 | 0 | 0.43 | 0.57 |

* No sample.

— One liquid phase.

Source: ESE, 1984.

toward the top apex of the triangle, as shown by the arrows. Titration was continued through the 2-phase region until solids appeared, further defining the boundary between the 2-phase and 3-phase regions.

In the second set of titrations, binary mixtures of acetone and TNT corresponding to Points F, G, H, I, and J in Figure 4-1 were titrated with water until cloudiness was observed.

In order to establish the boundaries between the 3-phase region and the two 2-phase regions, published phase diagrams were examined. The naphthalene/acetone/water system exhibits phase behavior similar to that of TNT/acetone/water. The 3-phase region in Figure 2-1 bounded by Lines EB, BC, and CE was defined by analogy with the acetone/water/naphthalene system discussed by Francis (1963). It was assumed that TNT does not complex with water or acetone, so Lines EB and CE end at the apex representing pure TNT.

There are three separate regions of 2-phase equilibria in the TNT/acetone/water system. Two regions of liquid-solid equilibria are bounded by Points A, B, and E and by Points C, D, and E. In these two regions, solid TNT is in equilibrium with saturated liquid. In the 2-phase liquid-liquid region, a water-rich liquid is in equilibrium with a TNT-rich liquid, neither of which is saturated with TNT.

For the purpose of designing a solvent leaching system, the 1-phase region is most important. All compositions in this region exist as a single liquid phase.

The solubility curve for TNT as a function of acetone/water ratio in the solvent is shown in Figure 4-2 on rectangular coordinates. The curve diverges at 53-percent acetone in solvent. The top branch is the total solubility of TNT in the two phases. It should be noted that because saturated solutions with 53-percent to 91-percent acetone in the solvent

split into two phases, this line is calculated by combining the TNT in the separate phases. Single liquids corresponding to this line do not exist.

The lower of the two lines is the boundary between 1-phase and 2-phase behavior. The area below this line represents the range of good operation for a solvent leaching process. It can be seen that the solubility of TNT does not increase substantially until the acetone fraction in the solvent is greater than 40 percent. The solubility is highest between 80-percent and 100-percent acetone.

4.1.2 DNT Solubility

Analytical results of the DNT solubility experiments are listed in Table 4-2. The phase equilibrium diagram (Figure 4-3) is similar to that for TNT/acetone/water. The point at which two liquid phases appear is shifted to the left and the 2-phase region is smaller, but the phase diagram exhibits the same features.

The DNT/acetone/water phase diagram was developed in the same manner as the TNT/acetone/water phase diagram. The DNT saturation line was determined from the solubility tests. The shape of the boundary between the two liquid phases and the 1-phase region is the result of titration experiments. The boundaries between the two separate liquid-solid regions and the 3-phase region result from the assumption that no DNT/water or DNT/acetone complexes occur.

The solubility curve for DNT as a function of acetone/water ratio in the solvent is shown in Figure 4-4. The 2-liquid-phase region extends from 50-percent to 91-percent acetone in the solvent. Again, the position of the upper curve was calculated from the composition and relative amounts of the water-rich phase and DNT-rich phase. As with TNT, the solubility of DNT does not increase appreciably until the concentration of acetone in the solvent exceeds 40 percent.

Table 4-2. DNT Solubility in Acetone/Water

| Initial Weight- Percent Acetone | Water-Rich Fractions | | | | DNT-Rich Fractions | | | |
|--|----------------------|-----------------|---------|--------|--------------------|-----------------|---------|------|
| | Volume Percent | Weight Fraction | | | Volume Percent | Weight Fraction | | |
| | | Water | Acetone | DNT | | Water | Acetone | DNT |
| 0 | 100 | 100 | 0 | 0.0002 | 0 | — | — | — |
| 33 | 100 | 0.65 | 0.35 | 0.0004 | 0 | — | — | — |
| 50 | 100 | 0.49 | 0.49 | 0.02 | 0 | — | — | — |
| 67 | 46.1 | 0.44 | 0.51 | 0.05 | 53.9 | 0.05 | 0.49 | 0.46 |
| 80 | 11.9 | 0.48 | 0.47 | 0.05 | 88.1 | 0.05 | 0.48 | 0.47 |
| 90 | Trace | * | * | * | <100 | 0.03 | 0.49 | 0.48 |
| 100 | 0 | — | — | — | 100 | 0 | 0.43 | 0.57 |

* No sample.

— One liquid phase.

Source: ESE, 1984.

4.1.3 Tetryl Solubility

Results of the tetryl solubility experiments are listed in Table 4-3 and graphically depicted in Figure 4-5. The tetryl/acetone/water system does not exhibit liquid-liquid 2-phase behavior. All of the saturated solutions exist as a single liquid in equilibrium with solid tetryl.

Table 4-3. Tetryl Solubility in Acetone/Water

| | Weight Fraction | | | | | | |
|--------------------|-----------------|-------|-------|-------|-------|-------|-------|
| Acetone in Solvent | 0 | 0.33 | 0.50 | 0.67 | 0.80 | 0.90 | 1.00 |
| Tetryl in Solution | 0.00003 | 0.001 | 0.009 | 0.071 | 0.204 | 0.314 | 0.397 |

Source: ESE, 1984.

It can be seen from Figure 4-5 that tetryl is sparingly soluble in acetone/water mixtures with less than 50-percent acetone. The solubility increases rapidly with increasing acetone concentration in the solvent after this point.

4.1.4 RDX Solubility

The solubility of RDX in acetone/water mixtures is shown in Table 4-4 and Figure 4-6. This system does not exhibit liquid-liquid 2-phase behavior.

Table 4-4. RDX Solubility in Acetone/Water

| | Weight Fraction | | | | | | |
|--------------------|-----------------|-------|-------|-------|-------|-------|-------|
| Acetone in Solvent | 0 | 0.33 | 0.50 | 0.67 | 0.80 | 0.90 | 1.00 |
| Tetryl in Solution | 0.00004 | 0.001 | 0.006 | 0.020 | 0.048 | 0.069 | 0.085 |

Source: ESE, 1984.

As with the other explosives studied, the solubility of RDX is very low in acetone/water mixtures with less than 50-percent acetone. The solubility increases monotonically to a maximum at 100-percent acetone.

4.2 MULTICOMPONENT SOLUBILITY

To determine whether there is competition for solubilization among the explosives, acetone/water mixtures were saturated with all four of the explosives simultaneously (a 6-component system). If competition occurs, one or several of the compounds could be precipitated out as others dissolve.

The results of the multicomponent experiments are shown in Table 4-5. Material balances, calculated for each sample for all four explosives, showed that all samples contained excess solid phase of all explosives, with the exception of the 67-percent acetone fraction and the 80-percent acetone fraction. These two samples were saturated with RDX and tetryl but not with TNT or DNT. The top phase of the 90-percent acetone fraction was too small to sample.

It can be seen in Table 4-5 that the bottom phase of the 33-, 50-, and 90-percent acetone fractions had 95-percent acetone in the solvent. The top phase of the 33- and 50-percent fractions had approximately 18-percent acetone in the solvent. Concentrations of the explosives in all bottom phases were the same within experimental error. Explosives concentrations in the top phase were also the same.

Thus, the 6-component system behaves in the same manner as the DNT and TNT ternary systems. The explosives concentration data are plotted on rectangular coordinates in Figures 4-7 through 4-10. These graphs indicate that all saturated 6-component mixtures with acetone concentrations in the initial solvent between 18 percent and 95 percent will form two liquid phases with constant compositions.

Table 4-5. Solubility of Explosives in Multicomponent System

| Fraction | Parameter | Weight Fraction | | | | Acetone in Solvent |
|--------------|-----------|-----------------|---------|---------|---------|--------------------|
| | | RDX | Tetryl | TNT | DNT | |
| 0 | X | 0.00005 | 0.00001 | 0.00009 | 0.00015 | 0 |
| | X' | 0.00005 | 0.00001 | 0.00009 | 0.00015 | |
| 33 | X | 0.00014 | 0.00003 | 0.00033 | 0.00058 | 0.16 |
| Top Phase | X' | 0.00014 | 0.00003 | 0.00032 | 0.00057 | |
| 33 | X | 0.021 | 0.049 | 0.372 | 0.413 | 0.95 |
| Bottom Phase | X' | 0.126 | 0.253 | 0.720 | 0.741 | |
| 50 | X | 0.00019 | 0.00004 | 0.00043 | 0.00080 | 0.19 |
| Top Phase | X' | 0.00019 | 0.00004 | 0.00043 | 0.00080 | |
| 50 | X | 0.025 | 0.031 | 0.372 | 0.413 | 0.95 |
| Bottom Phase | X' | 0.134 | 0.163 | 0.701 | 0.722 | |
| 67 | X | 0.00044 | 0.00006 | 0.00078 | 0.00151 | 0.25 |
| Top Phase | X' | 0.00044 | 0.00006 | 0.00078 | 0.00151 | |
| 67 | X | 0.029 | 0.026 | 0.343 | 0.371 | 0.96 |
| Bottom Phase | X' | 0.111 | 0.100 | 0.597 | 0.616 | |
| 80 | X | 0.00033 | 0.00006 | 0.00057 | 0.00117 | 0.22 |
| Top Phase | X' | 0.00033 | 0.00006 | 0.00057 | 0.00113 | |
| 80 | X | 0.025 | 0.063 | 0.352 | 0.405 | 0.95 |
| Bottom Phase | X' | 0.142 | 0.291 | 0.696 | 0.725 | |

Table 4-5. Solubility of Explosives in Multicomponent System (Continued, Page 2 of 2)

| Fraction | Parameter | Weight Fraction | | | | |
|--------------|-----------|-----------------|--------|-------|-------|--------------------|
| | | RDX | Tetryl | TNT | DNT | Acetone in Solvent |
| 90 | X | 0.024 | 0.051 | 0.375 | 0.391 | 0.95 |
| Bottom Phase | X' | 0.132 | 0.240 | 0.701 | 0.709 | |
| 100 | X | 0.026 | 0.052 | 0.363 | 0.423 | 100 |
| | X' | 0.158 | 0.274 | 0.726 | 0.755 | |

NOTE: X = Weight fraction of individual explosive in solution.

X' = Weight fraction of individual explosive in solution (other-explosives-free basis).

Source: ESE, 1984.

Weight fractions of all individual explosives in the saturated multicomponent systems are less than weight fractions in the respective ternary explosive/acetone/water solutions. However, the amount of final solution obtained from a given amount of initial solvent is much larger in the multicomponent system than in the ternary system. For example, the 100-percent acetone solvent sample started as 4 milliliters (ml) of acetone, with a density of 0.8 gram per cubic centimeter (gm/cc). The final saturated solution was 21 ml, with a density of 1.3 gm/cc. The solution was viscous and contained 86-percent total explosives. The bottom phase of the saturated 2-phase samples contained 84-percent total explosives.

To eliminate this effect and compare solubilities in the multicomponent system to those in the individual ternary systems, the concentrations were calculated on an "other-explosives-free" basis. This parameter, X' , is defined as the weight of the individual explosive of interest, divided by the sum of that explosive plus acetone plus water.

For example: $X'_{\text{TNT}} = (\text{grams of TNT}) / (\text{grams of TNT} + \text{acetone} + \text{water})$.

This parameter is plotted with the corresponding ternary solubility data in Figures 4-11 through 4-14. It can be seen in these figures that the weight of individual explosive per unit weight of solvent is significantly higher in the multicomponent systems than in the ternary systems for TNT, DNT, and RDX. The number of grams of tetryl per gram of solvent is approximately 40 percent lower in the multicomponent system.

This indicates TNT, DNT, and RDX are chemically compatible in solution and help solubilize each other. Tetryl is apparently less compatible in the multicomponent system and thus exhibits decreased solubility in the 6-component system.

4.3 LEACH RATE TESTS

The leach rate test results are shown in Figures 4-15 and 4-16. Only TNT concentrations were high enough to quantify in the Navajo AD and Ft. Wingate AD sediment tests. The levels of TNT, RDX, and tetryl were high enough to quantify in the Louisiana AAP leachate.

As shown in Figure 4-15, TNT concentrations in the Ft. Wingate AD and Navajo AD leachates reached steady-state conditions before the first 10-minute period ended. The Louisiana AAP leachate, which is much more concentrated than the other two leachates, took 20 to 30 minutes to approach steady-state conditions, as shown in Figure 4-16.

4.4 COUNTERCURRENT EXTRACTION

4.4.1 Ft. Wingate AD Sediment

The results of the 4-stage countercurrent extraction of Ft. Wingate AD sediment are shown schematically in Figure 4-17. The circles represent contact stages, and the individual stage efficiencies are shown within the circles. Parameters which characterize each of the liquid and sediment streams are also shown.

Only TNT was present in sufficient levels for removal efficiencies to be calculated. The feed sediment (S_F) contained 1,240 mg/kg TNT on a dry-weight basis. The first contact stage reduced the sediment TNT concentration to 141 mg/kg, for a 1-stage removal efficiency of 88.6 percent. After 2 stages, the TNT concentration was 23.5 mg/kg, giving a 2-stage removal of 98.1 percent. After 3 stages, the TNT concentration was 8.1 mg/kg, a 3-stage removal of 99.3 percent. After 4 contact stages, the final extracted solid (S_4) contained 6.0 mg/kg of TNT, which represents 99.5-percent overall removal efficiency.

The final extract (L_1) was 90.6-percent acetone and 9.4-percent water. The extract contained 260 milligrams per liter (mg/l) of TNT. Referring to Figure 4-1, it can be seen that this concentration is well below the

solubility limit of TNT and well out of the 2-liquid-phase region. In fact, no liquid-liquid 2-phase behavior was observed in the extract.

The normalized TNT concentration in the liquid is plotted against liquid stream number in Figure 4-18. The TNT concentration of each stream is normalized by dividing its value by the value in L_1 . The data presented in Figure 4-18 show that, as expected in countercurrent processes, most of the solute is transferred to the liquid in the first stage.

In Figure 4-19, the normalized liquid TNT concentrations for L_2 , L_3 , and L_4 are shown. The upper curve represents the measured experimental data. The lower curve represents calculated concentrations that can be attributed to entrainment of liquid with the solid stream. The purpose of Figure 4-19 is to determine whether adsorption of TNT on the inert substrate will be a major consideration in process design. As would be expected, entrainment causes most of the stage inefficiency. However, adsorption is probably the main cause of the low removal efficiency in Stage 4, because of the low entering concentration of explosives.

It should be noted that some of the apparent adsorption effect could be caused by inaccuracies in the percent-moisture determinations. After filtering of the leached sediment, the acetone solvent evaporated rapidly, and accurate moisture values were difficult to obtain.

Figure 4-20 is a plot of normalized TNT concentrations in the sediment-versus-sediment stream number. It can be seen that most of the TNT was removed in the first stage, and removal decreases with subsequent stages. While the removal efficiencies in Stage 1 and Stage 2 were similar, Stage 1 removed more than 9 times as much TNT as Stage 2.

The results of a settling test performed with Ft. Wingate AD sediment are shown in Figure 4-21. The vertical axis represents normalized sludge height and the horizontal axis represents time. The normalized sludge

height is the height of the sludge/clear liquid interface at time "t" divided by the initial sludge height ($t=0$).

On this figure the classical settling regimes can be seen. The settling velocity in the free settling regime is 0.5 centimeter per minute. The total suspended solids (TSS) content of the supernatant was 100 mg/l.

4.4.2 Navajo AD Sediment

The results of the 4-stage countercurrent extraction of Navajo AD sediment are shown in Figure 4-22. The circles represent contact stages, and the stage efficiencies are shown within the circles. Liquid and sediment parameters are also presented.

As with the Ft. Wingate AD sediment, only TNT was present in sufficient quantities to calculate removal efficiencies. The feed sediment (S_F) contained 19,300 mg/kg (1.9 percent) of TNT on a dry-weight basis. The first stage reduced the sediment TNT concentration to 2,350 mg/kg. This is a 1-stage removal of 87.8 percent. After 2 stages, the TNT concentration was 231 mg/kg, giving a 2-stage removal of 98.8 percent. After 3 stages, the TNT concentration was 40.3 mg/kg, a 3-stage removal of 99.8 percent. The final extracted solid (S_4) contained 7.0 mg/kg of TNT. The overall removal efficiency was 99.96 percent.

The final extract (L_1) was 90.9-percent acetone and 8.6-percent water. The extract contained 5,500 mg/l of TNT, which is well below saturation and outside the 2-liquid-phase region.

The normalized TNT concentration in the liquid is plotted against liquid stream number in Figure 4-23. This figure shows that, as with Ft. Wingate AD sediment, most of the TNT was dissolved in the first stage.

Figure 4-24 is a graph of the relative contribution of entrainment and adsorption in decreasing the extraction stage efficiencies. The TNT concentration in the Navajo AD sediment entering Stage 4 is much higher than in the Ft. Wingate AD sediment entering Stage 4 (40.3 mg/kg versus 8.1 mg/kg). At the higher TNT concentration, adsorption does not have as great a detrimental effect on efficiency, so Stage 4 efficiency is 80.0 percent.

Figure 4-25 is a plot of normalized TNT concentration as a function of stage number for the Navajo AD sediment experiments. Most of the TNT was removed in the first stage. Removal efficiencies per stage were approximately 90 percent for Stage 1 and Stage 2 and approximately 80 percent for Stage 3 and Stage 4.

A settling test was performed on the Navajo AD sediment. The curve, shown in Figure 4-26, has the same characteristics as the curve for the Ft. Wingate AD sediment settling test. The free settling velocity is 1.3 centimeters per minute. The supernatant TSS was 50 mg/l.

4.4.3 Louisiana AAP Sediment

The sediment obtained from Louisiana AAP contained approximately 98 dry-weight-percent explosives. One of the main criteria for design of the countercurrent extraction experiment is that the amount of inerts must be large enough to analyze after leaching. If the Louisiana AAP sediment were used as obtained, a large amount of sediment and acetone would be required. In addition, previously reported levels of explosives in Louisiana AAP sediments were much lower than levels in these samples, so the sediment was mixed with clean soil to approximately 40-percent explosives.

The results of the 4-stage countercurrent extraction of Louisiana AAP sediment are shown schematically in Figure 4-27. Only TNT concentrations in the sediment were high enough to follow through all 4 stages. The

removal efficiencies shown on Figure 4-27 are for TNT. RDX could be quantified in S_F , S_1 , and S_2 . Stage 1 and Stage 2 RDX removal efficiencies are, respectively, 89.0 percent and 98.5 percent. TNB was quantified in S_F and S_1 . Stage 1 removal efficiency for TNB was 88.8 percent.

These results show that stage efficiencies are relatively independent of the compound on which the calculation is based. Stage 1 efficiencies were 89.8 percent, 89.0 percent, and 88.8 percent for TNT, RDX, and TNB, respectively. Stage 2 efficiencies were 98.9 and 98.5 percent for TNT and RDX, respectively.

The feed sediment (S_F) contained 38-percent TNT, 3.7-percent RDX, and 58-mg/kg TNB on a dry-weight basis. Using TNT as the basis for calculating cumulative efficiencies, the first stage removed TNT to 38,000 mg/kg for an 89.8-percent removal. The sediment from Stage 2 contained 430 mg/kg TNT. This is a 2-stage removal of 99.89 percent. After 3 stages, the TNT concentration was 83 mg/kg, giving a 3-stage removal efficiency of 99.98 percent. The final extracted sediment contained 17.3 mg/kg of TNT and undetectable levels of RDX and TNB, which represents 99.995-percent removal based on TNT concentration. If the removal were based on the change of the weight of TNT rather than the change in concentration, the removal efficiency would be 99.998 percent.

The final extract (L_1) is 83.0-percent acetone, 6.2-percent water, 9.8-percent TNT, 1.0-percent RDX, and 32-mg/kg TNB on a weight basis. The solvent, excluding explosives, is 93.2-percent acetone and 6.8-percent water. The concentration of TNT is well below its individual saturation level in 93.2-percent acetone.

The concentration of RDX calculated on a TNT-free and TNB-free basis is 1.1 weight-percent in L_1 . Referring to Figure 4-13, it can be seen that this concentration is above the solubility limit of RDX in 93.2-percent

acetone in the ternary system. However, 1.1 percent does not exceed the enhanced multicomponent solubility represented by X'_{RDX} in Figure 4-13.

Liquid-liquid 2-phase behavior was not observed in the extract. Water was added slowly to a sample of L_1 to determine whether 2 liquid phases would appear. The solution split into 2 liquid phases when the solvent was approximately 71-percent acetone and 29-percent water.

The normalized explosives concentration in the liquid extract is plotted against liquid stream number in Figure 4-28. Because the stage removal efficiencies were similar for all compounds that could be quantified, normalized concentrations fall along the same line.

Figure 4-29 shows the relative effects of entrainment and adsorption on stage inefficiencies, as discussed earlier. As with the Navajo AD sediment, entrainment dominates throughout.

Figure 4-30 is a plot of normalized TNT concentration in the sediment. The RDX and TNB concentrations follow the same line as far as they could be traced. These concentrations are consistent with the concentrations for Navajo AD sediment. Stage efficiencies are high throughout.

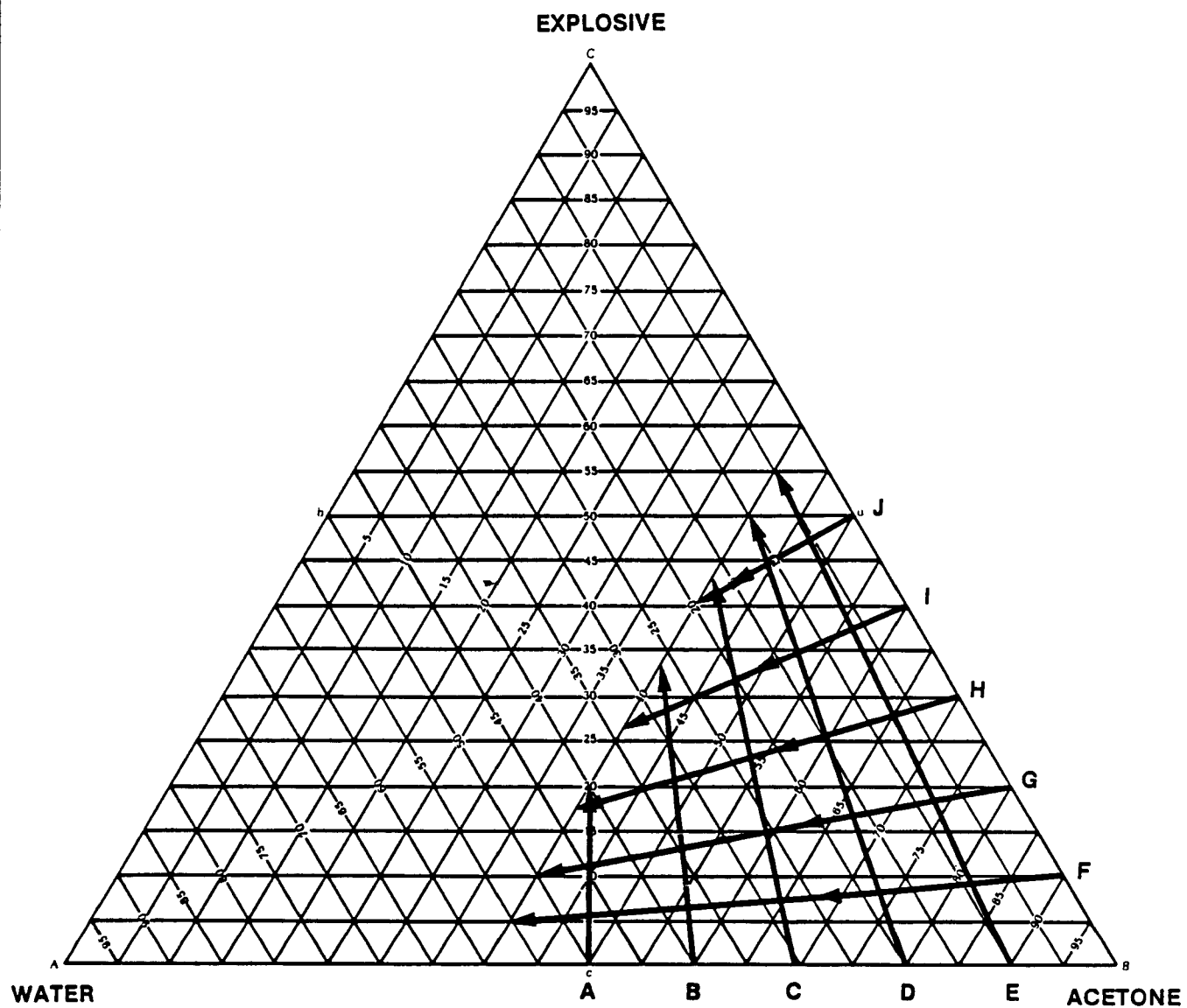
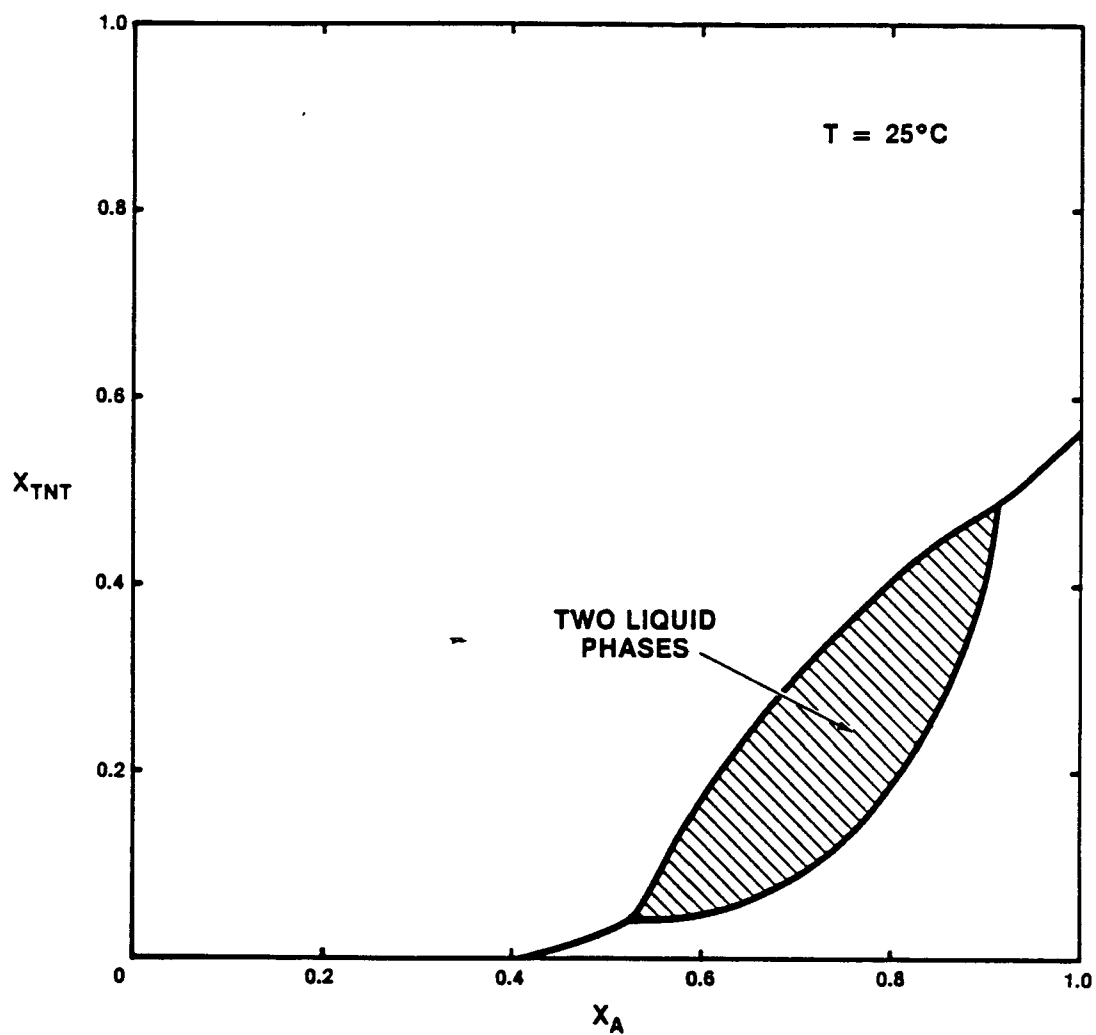


Figure 4-1
TITRATION EXPERIMENTS

SOURCE: ESE, 1984.

USATHAMA



X_A = WEIGHT FRACTION OF ACETONE (TNT-FREE BASIS)
 X_{TNT} = WEIGHT FRACTION OF TNT

Figure 4-2
SOLUBILITY OF TNT IN ACETONE/WATER

SOURCE: ESE, 1984.

USATHAMA

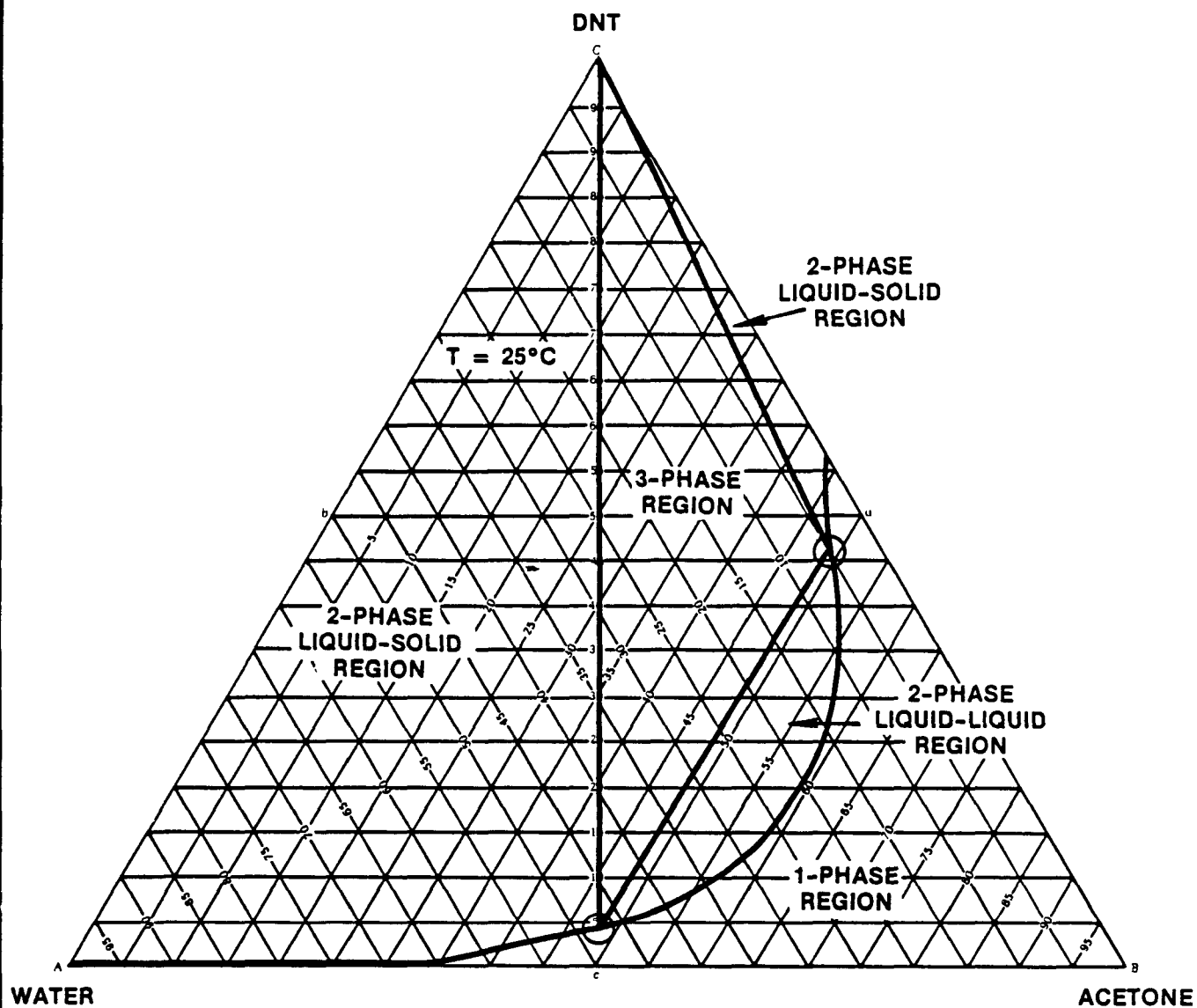
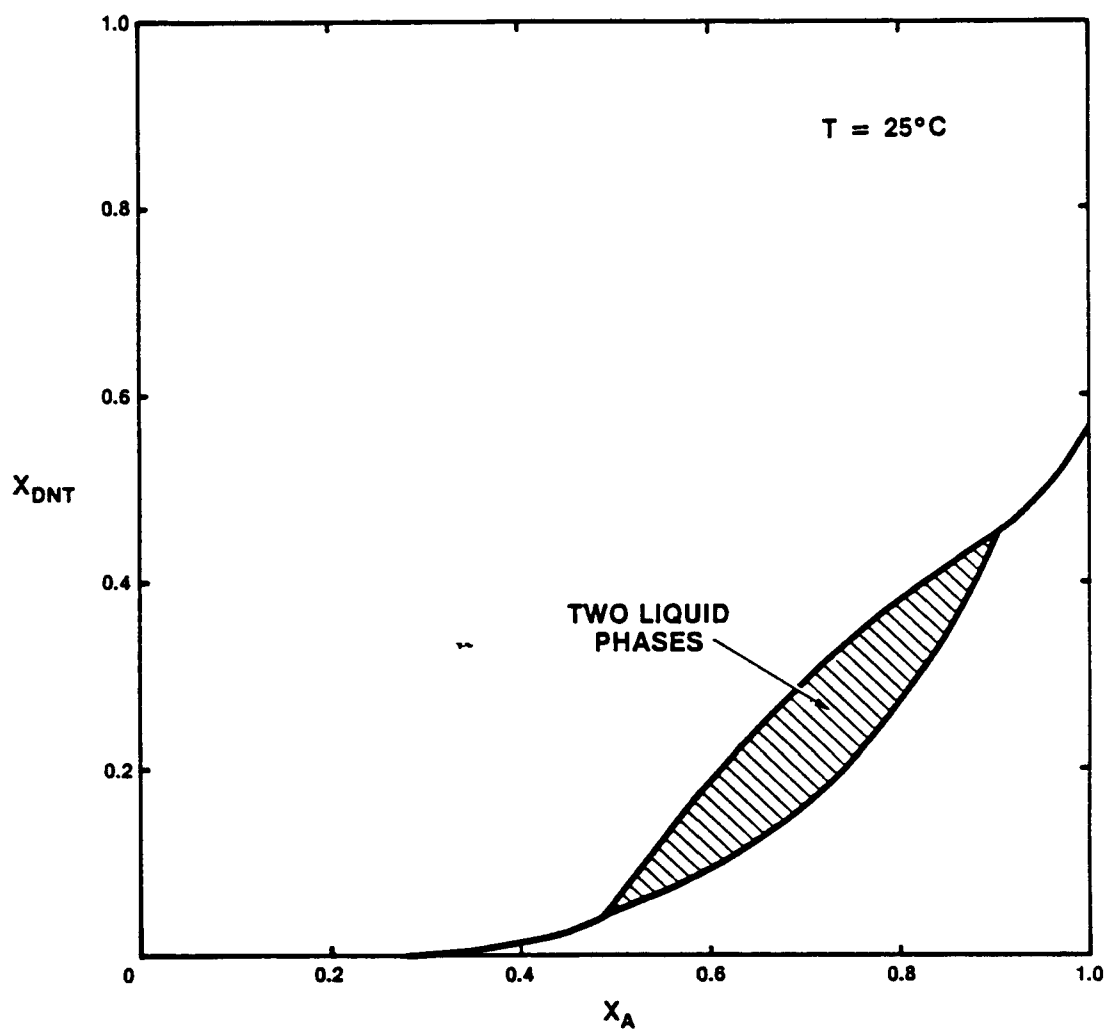


Figure 4-3
DNT/ACETONE/WATER PHASE DIAGRAM,
WEIGHT-FRACTION BASIS

SOURCE: ESE, 1984.

USATHAMA

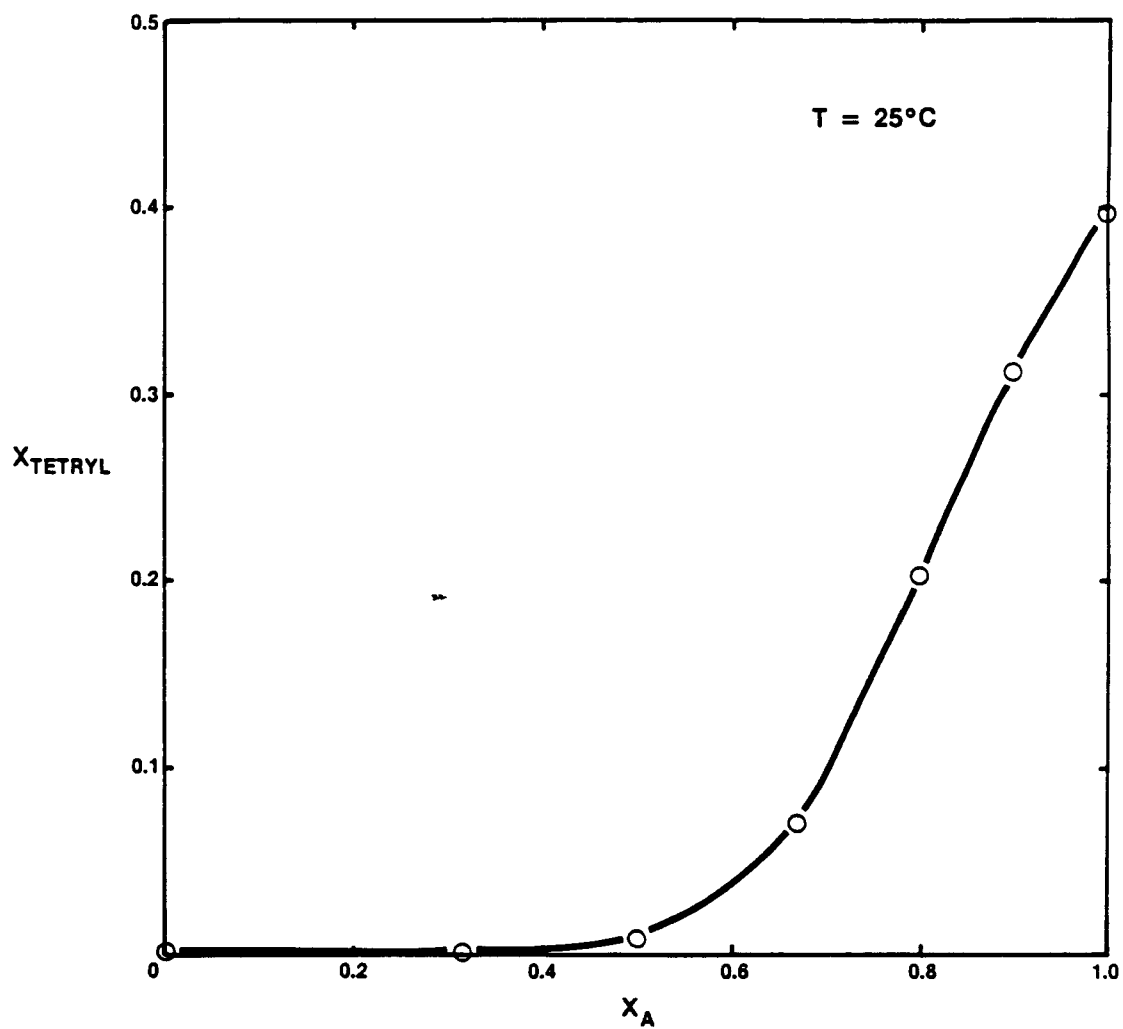


X_A = WEIGHT FRACTION OF ACETONE (DNT-FREE BASIS)
 X_{DNT} = WEIGHT FRACTION OF DNT

Figure 4-4
SOLUBILITY OF DNT IN ACETONE/WATER

SOURCE: ESE, 1984.

USATHAMA

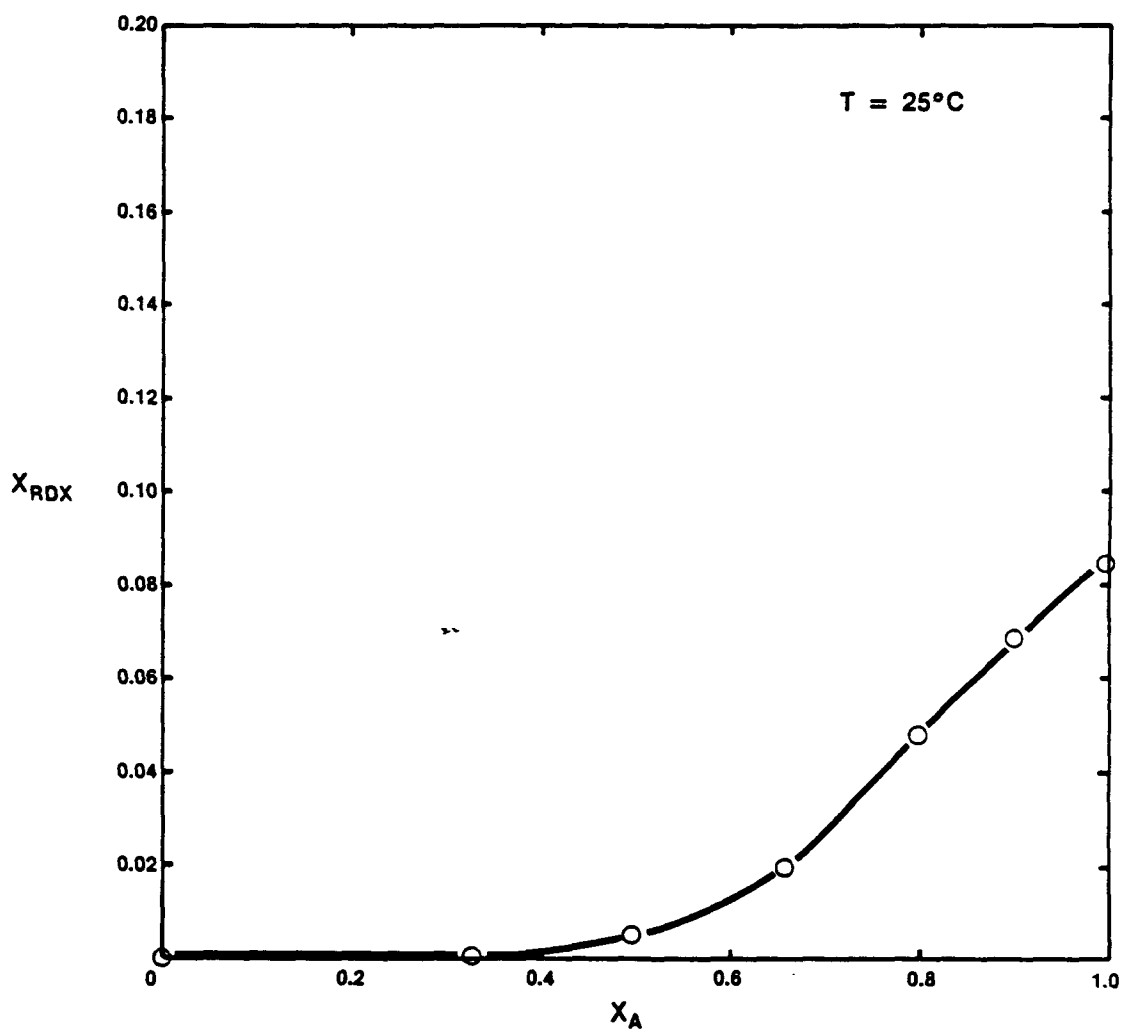


X_A = WEIGHT FRACTION OF ACETONE (TETRYL-FREE BASIS)
 X_{TETRYL} = WEIGHT FRACTION OF TETRYL

Figure 4-5
SOLUBILITY OF TETRYL IN
ACETONE/WATER

SOURCE: ESE, 1984.

USATHAMA

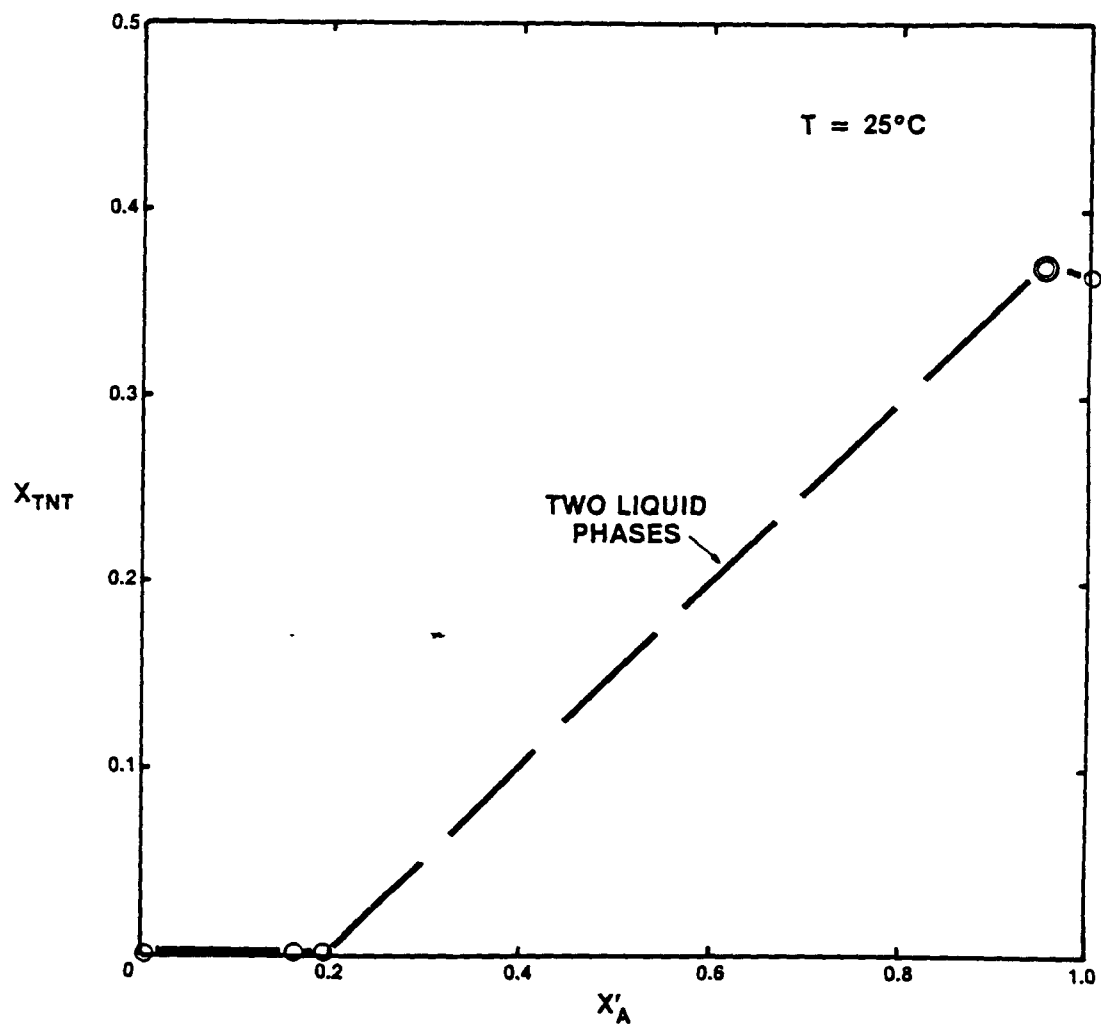


X_A = WEIGHT FRACTION OF ACETONE (RDX-FREE BASIS)
 X_{RDX} = WEIGHT FRACTION OF RDX

Figure 4-6
SOLUBILITY OF RDX IN ACETONE/WATER

SOURCE: ESE, 1984.

USATHAMA



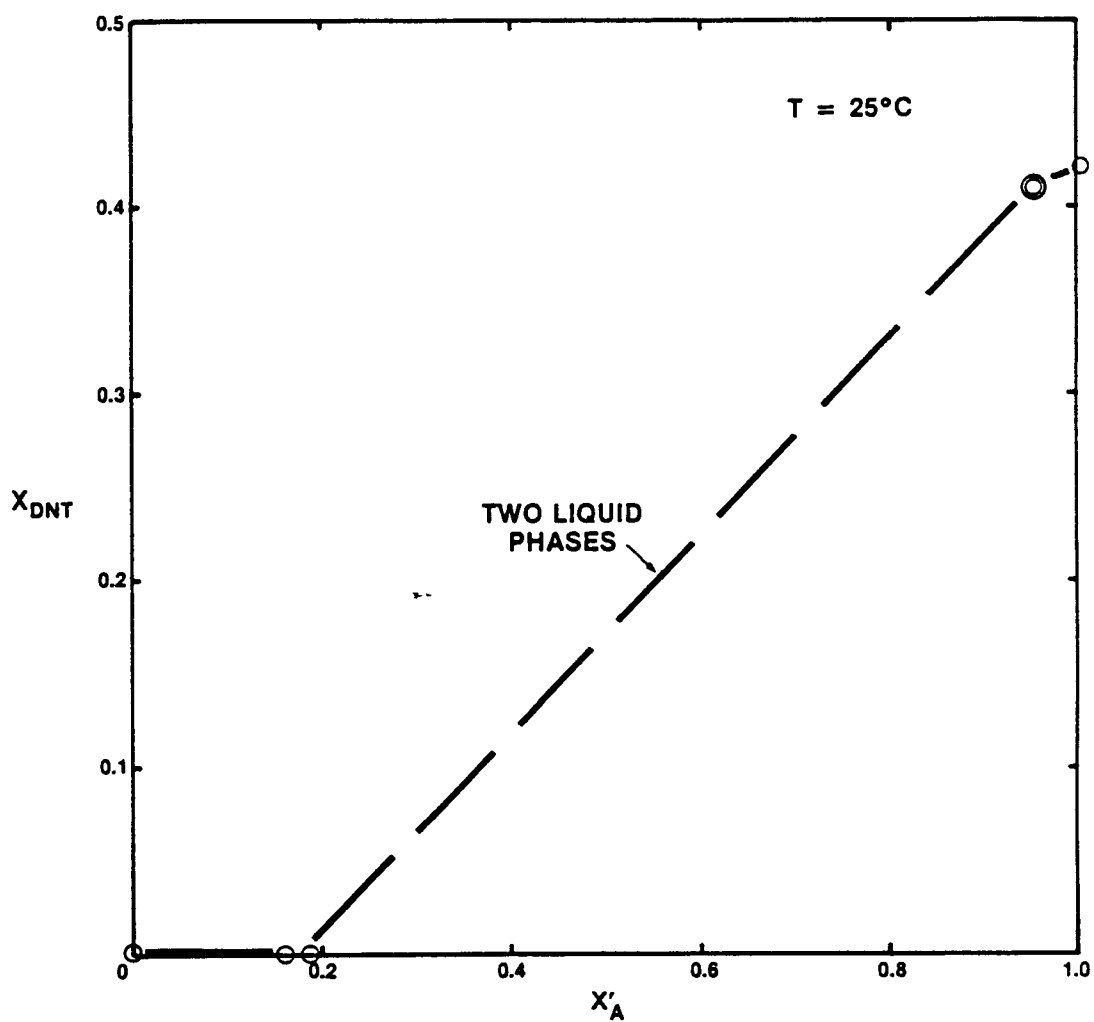
X'_A = WEIGHT FRACTION OF ACETONE IN SOLVENT
(EXPLOSIVES-FREE BASIS)

X_{TNT} = WEIGHT FRACTION OF TNT IN SOLUTION

Figure 4-7
SOLUBILITY OF TNT IN MULTICOMPONENT
SYSTEM

SOURCE: ESE, 1984.

USATHAMA



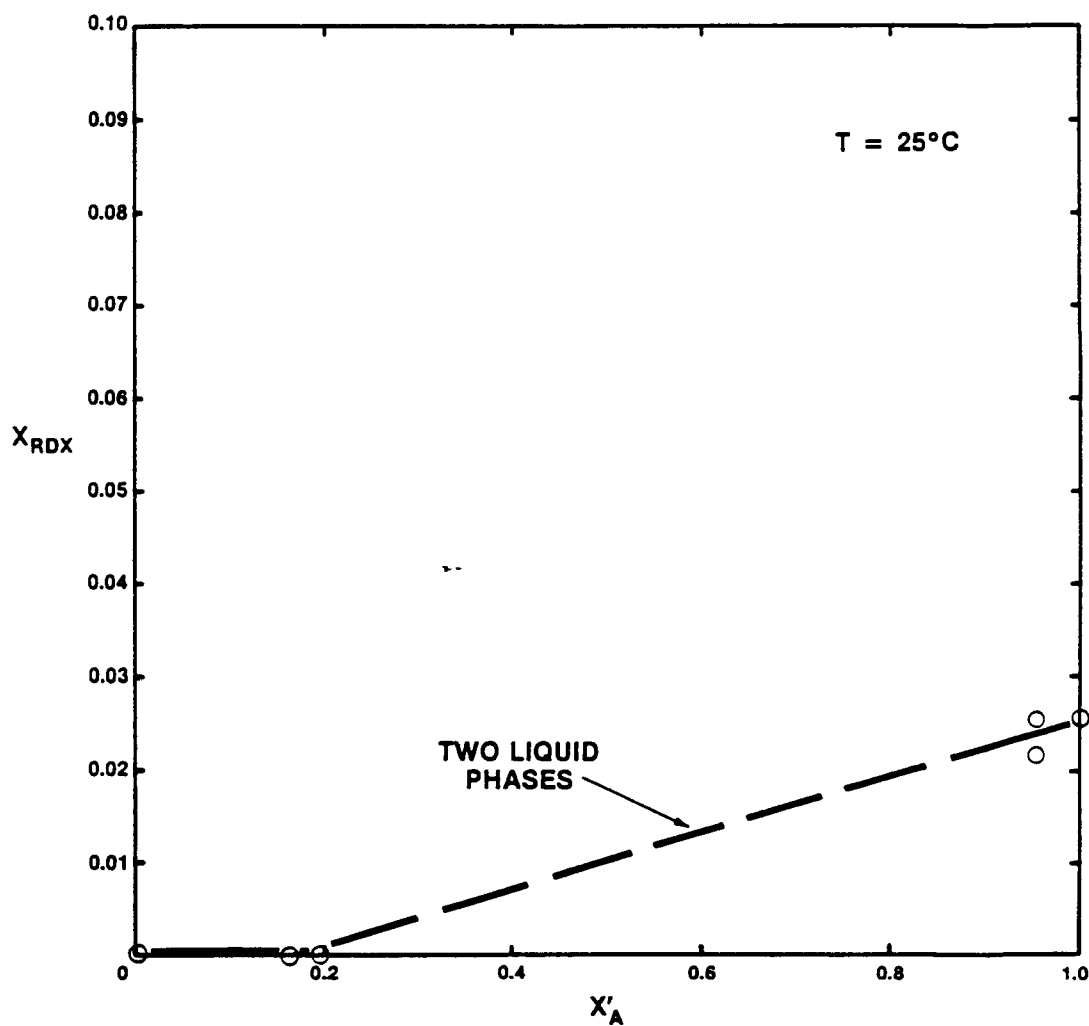
X'_A = WEIGHT FRACTION OF ACETONE IN SOLVENT
(EXPLOSIVES-FREE BASIS)

X_{DNT} = WEIGHT FRACTION OF DNT IN SOLUTION

Figure 4-8
SOLUBILITY OF DNT IN
MULTICOMPONENT SYSTEM

SOURCE: ESE, 1984.

USATHAMA



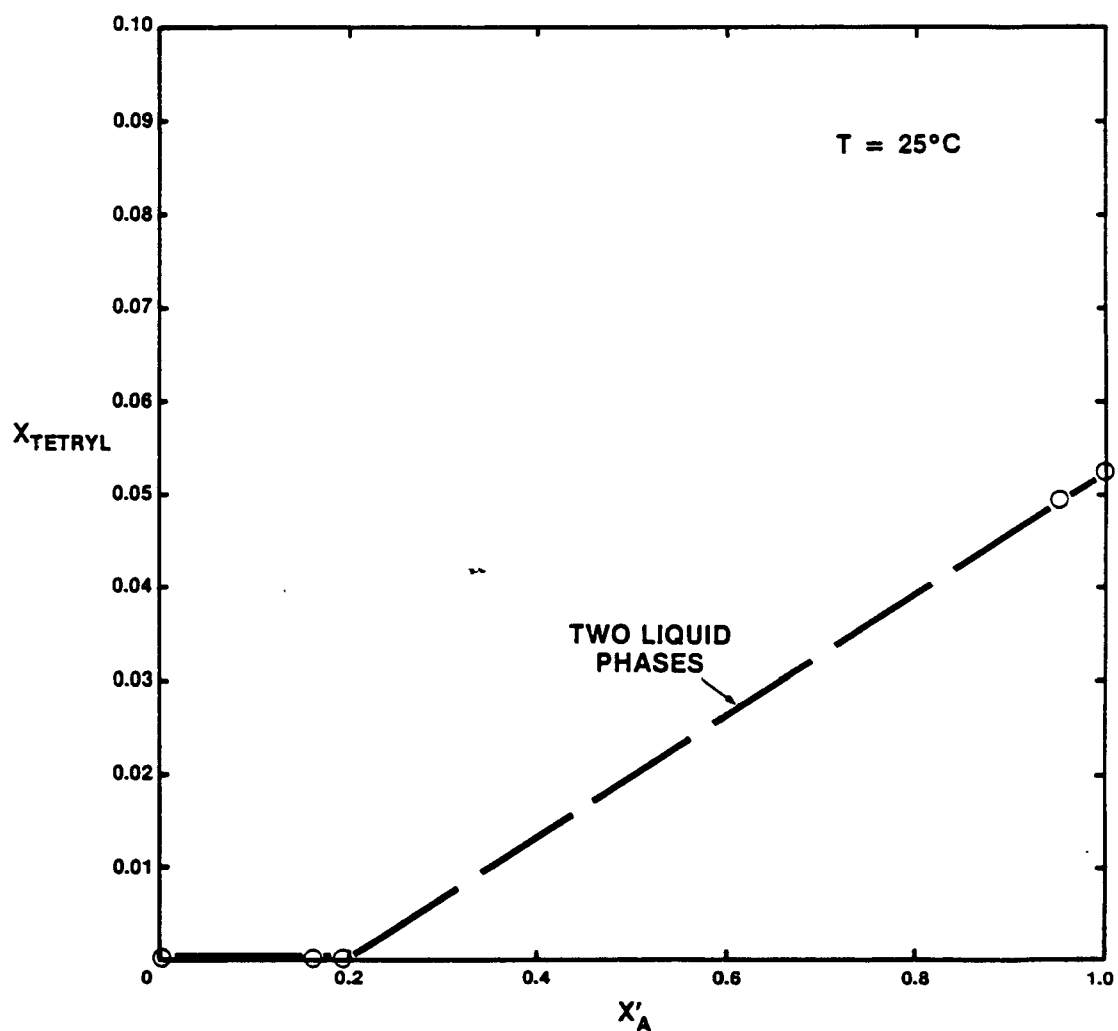
X'_A = WEIGHT FRACTION OF ACETONE IN SOLVENT
(EXPLOSIVES-FREE BASIS)

X_{RDX} = WEIGHT FRACTION OF RDX IN SOLUTION

Figure 4-9
SOLUBILITY OF RDX IN
MULTICOMPONENT SYSTEM

SOURCE: ESE, 1984.

USATHAMA



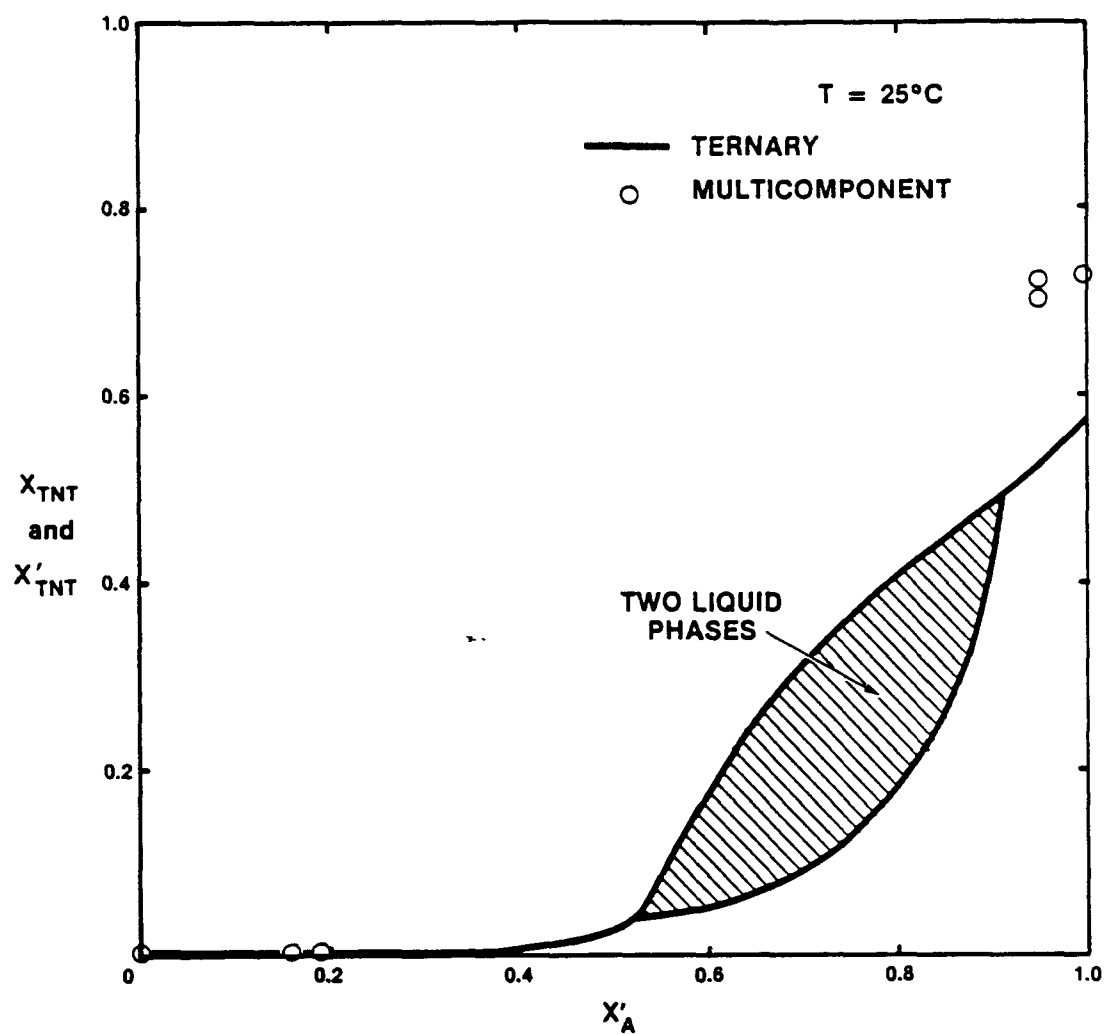
X'_A = WEIGHT FRACTION OF ACETONE IN SOLVENT
(EXPLOSIVES-FREE BASIS)

X_{TETRYL} = WEIGHT FRACTION OF TETRYL IN SOLUTION

Figure 4-10
SOLUBILITY OF TETRYL IN
MULTICOMPONENT SYSTEM

SOURCE: ESE, 1984.

USATHAMA



X'_A = WEIGHT FRACTION OF ACETONE IN SOLVENT
(EXPLOSIVES-FREE BASIS)

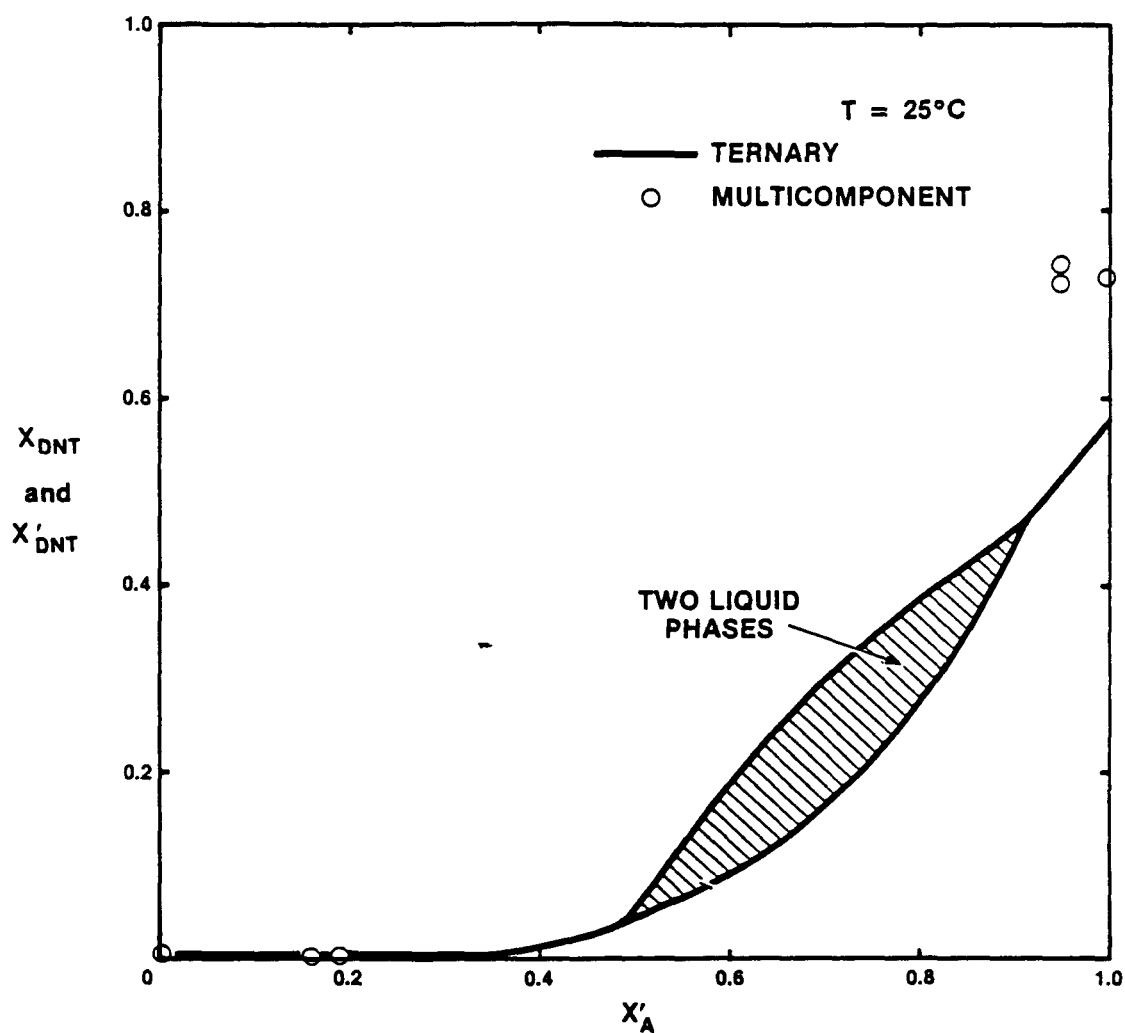
X_{TNT} = WEIGHT FRACTION OF TNT IN TERNARY SYSTEM

X'_{TNT} = WEIGHT FRACTION OF TNT IN MULTICOMPONENT SYSTEM
(OTHER-EXPLOSIVES-FREE BASIS)

Figure 4-11
COMPARISON OF TNT SOLUBILITY IN
TERNARY AND MULTICOMPONENT
SYSTEMS

SOURCE: ESE, 1984.

USATHAMA



X'_A = WEIGHT FRACTION OF ACETONE IN SOLVENT
(EXPLOSIVES-FREE BASIS)

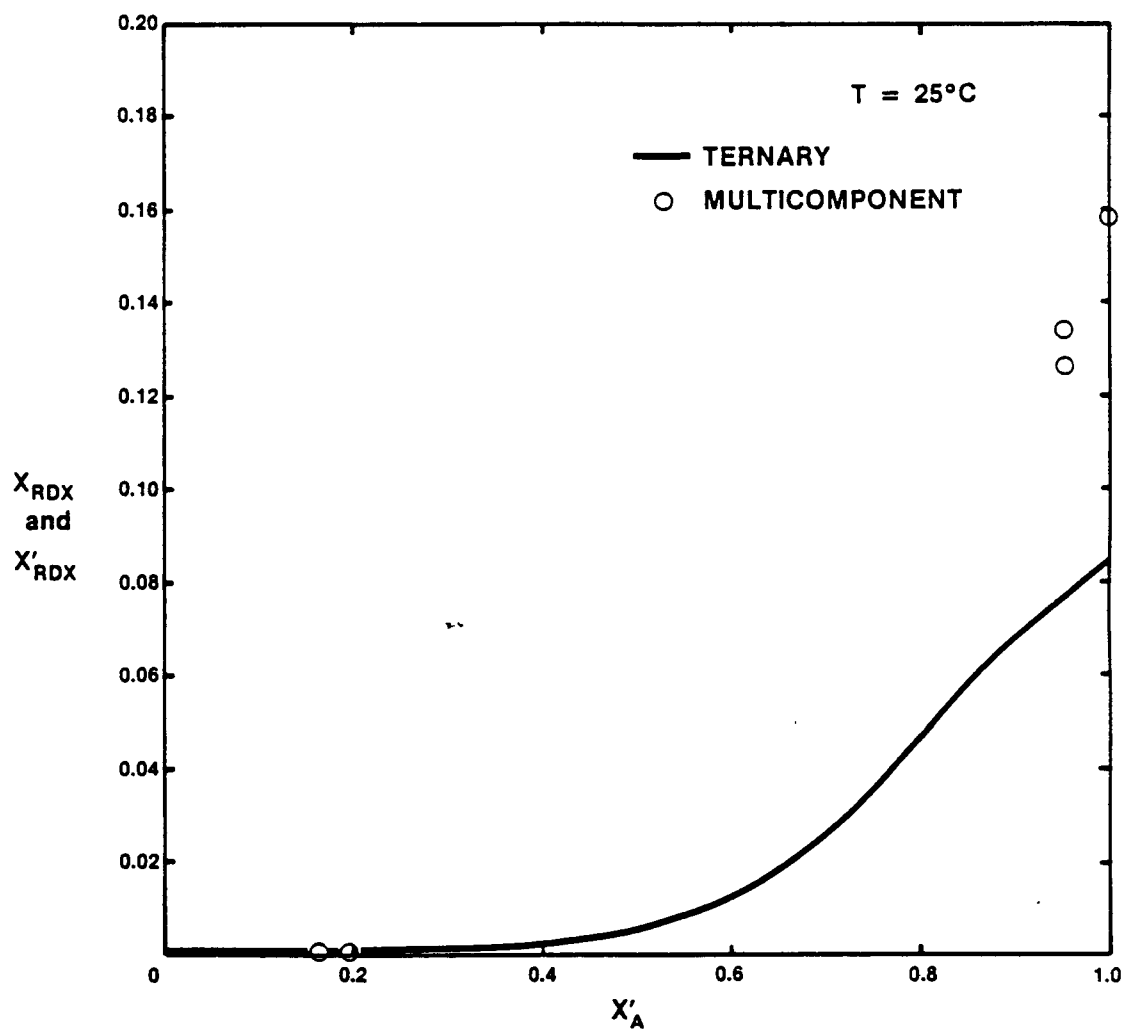
X_{DNT} = WEIGHT FRACTION OF DNT IN TERNARY SYSTEM

X'_{DNT} = WEIGHT FRACTION OF DNT IN MULTICOMPONENT SYSTEM
(OTHER-EXPLOSIVES-FREE BASIS)

Figure 4-12
COMPARISON OF DNT SOLUBILITY IN
TERNARY AND MULTICOMPONENT
SYSTEMS

SOURCE: ESE, 1984.

USATHAMA



X'_A = WEIGHT FRACTION OF ACETONE IN SOLVENT
(EXPLOSIVES-FREE BASIS)

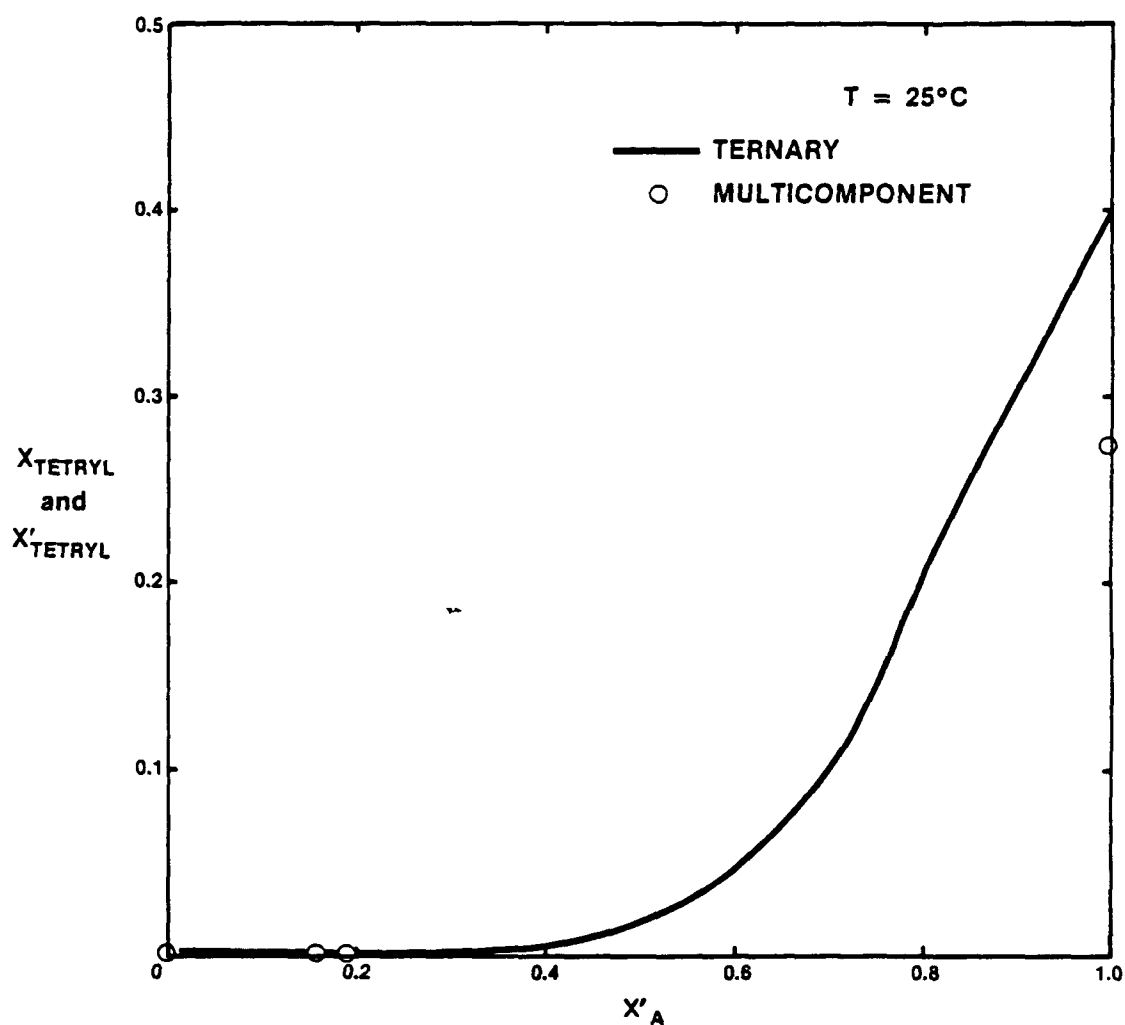
X_{RDX} = WEIGHT FRACTION OF RDX IN TERNARY SYSTEM

X'_{RDX} = WEIGHT FRACTION OF RDX IN MULTICOMPONENT SYSTEM
(OTHER-EXPLOSIVES-FREE BASIS)

Figure 4-13
COMPARISON OF RDX SOLUBILITY IN
TERNARY AND MULTICOMPONENT
SYSTEMS

SOURCE: ESE, 1984.

USATHAMA



X'_A = WEIGHT FRACTION OF ACETONE IN SOLVENT
(EXPLOSIVES-FREE BASIS)

X_{TETRYL} = WEIGHT FRACTION OF TNT IN TERNARY SYSTEM

X'_{TETRYL} = WEIGHT FRACTION OF TNT IN MULTICOMPONENT
SYSTEM (OTHER-EXPLOSIVES-FREE BASIS)

Figure 4-14
COMPARISON OF TETRYL SOLUBILITY IN
TERNARY AND MULTICOMPONENT
SYSTEMS

SOURCE: ESE, 1984.

USATHAMA

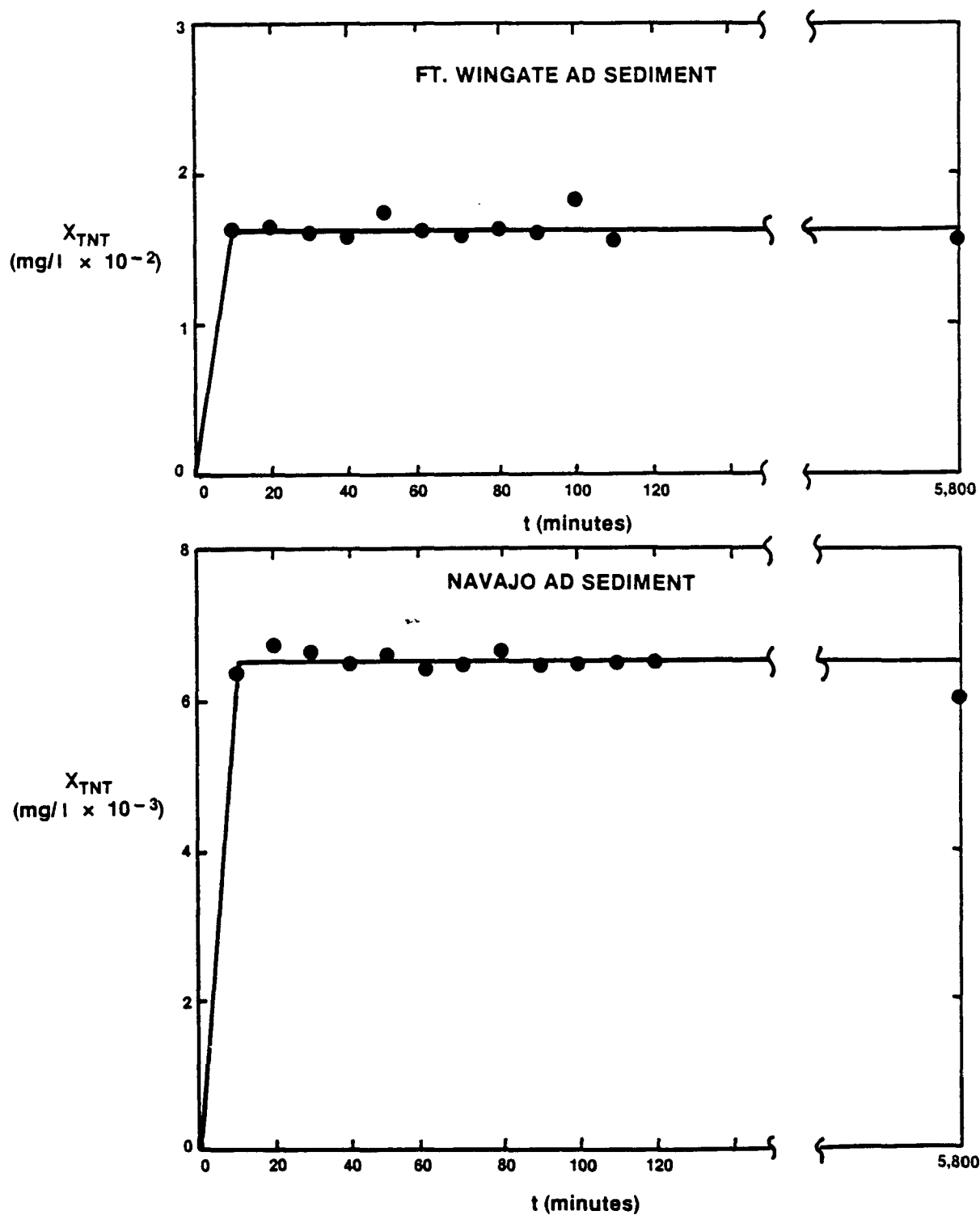


Figure 4-15
SEDIMENT LEACH RATE--FT.
WINGATE AD AND NAVAJO AD

SOURCE: ESE, 1984.

USATHAMA

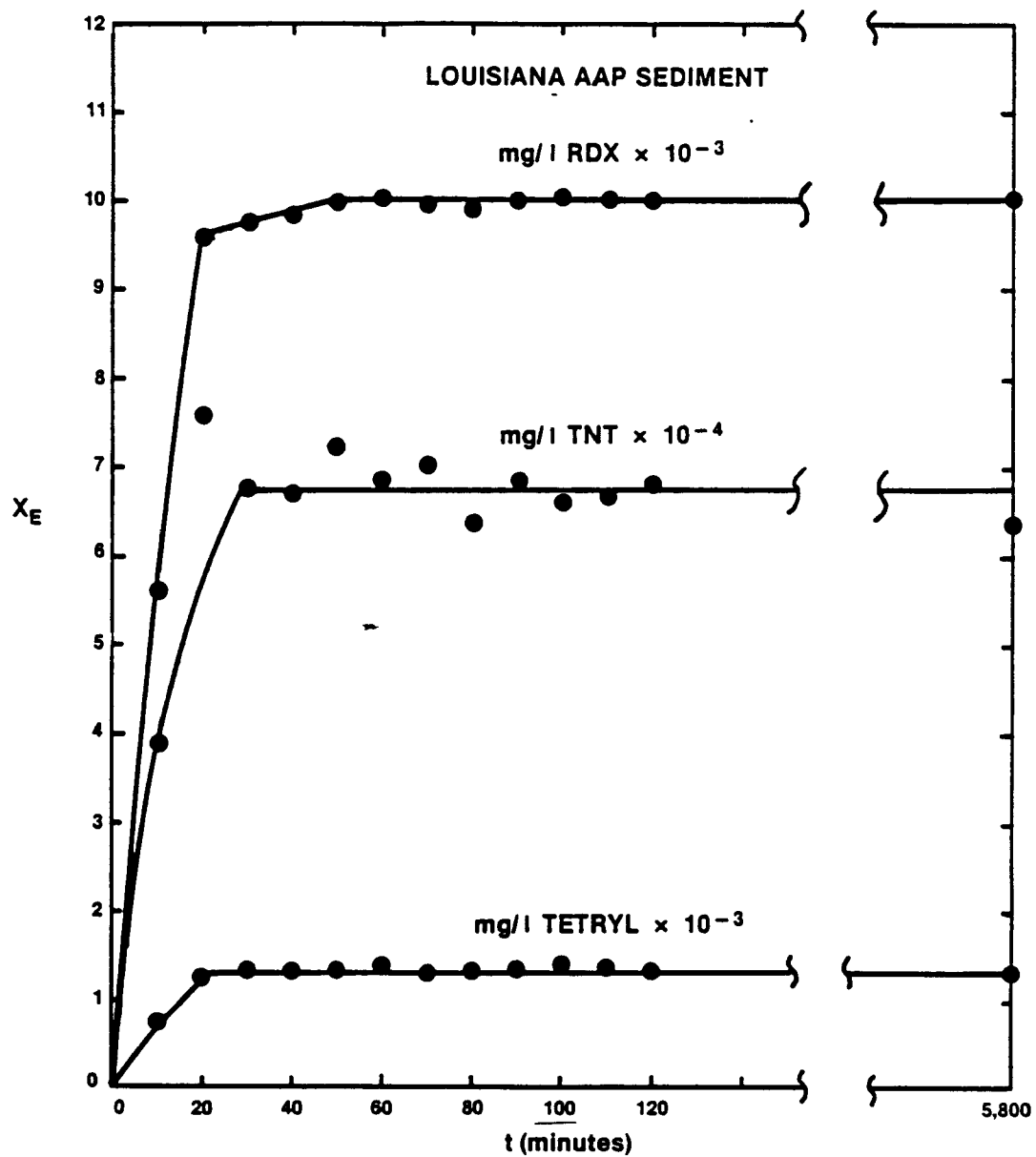
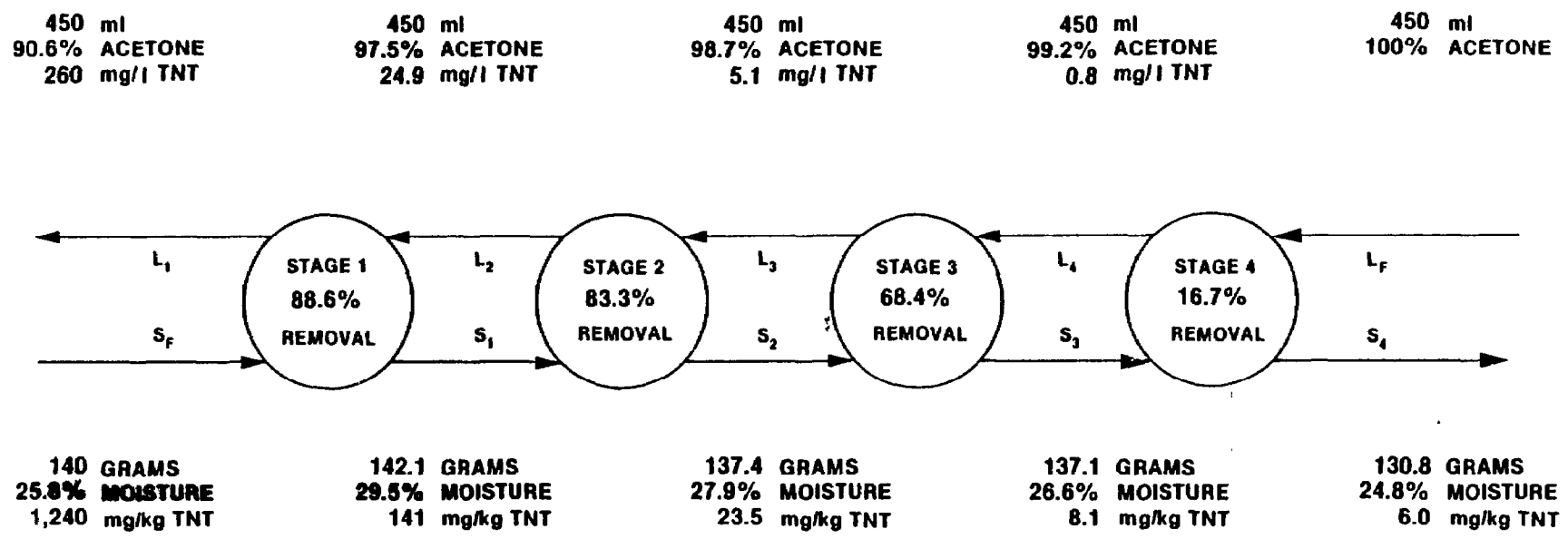


Figure 4-16
SEDIMENT LEACH RATE
--LOUISIANA AAP

SOURCE: ESE, 1984.

USATHAMA

4-33



OVERALL REMOVAL: 99.5%

~~#~~ DATA USED

Figure 4-17
COUNTERCURRENT EXTRACTION SIMULATION--FT. WINGATE AD

SOURCE: ESE, 1984.

USATHAMA

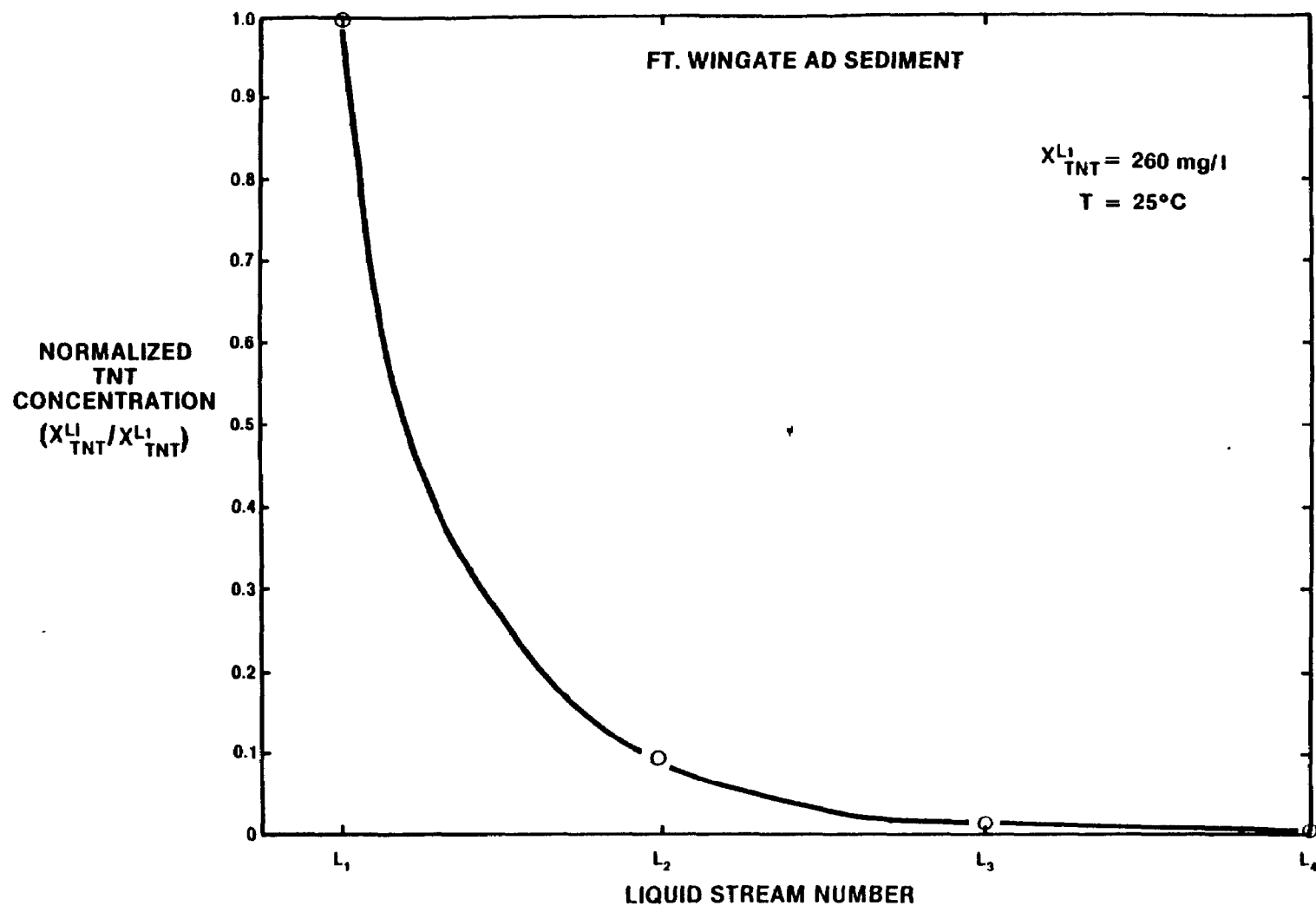


Figure 4-18
 NORMALIZED LIQUID TNT
 CONCENTRATION IN COUNTERCURRENT
 LEACHING -- FT. WINGATE AD

SOURCE: ESE. 1984.

USATHAMA

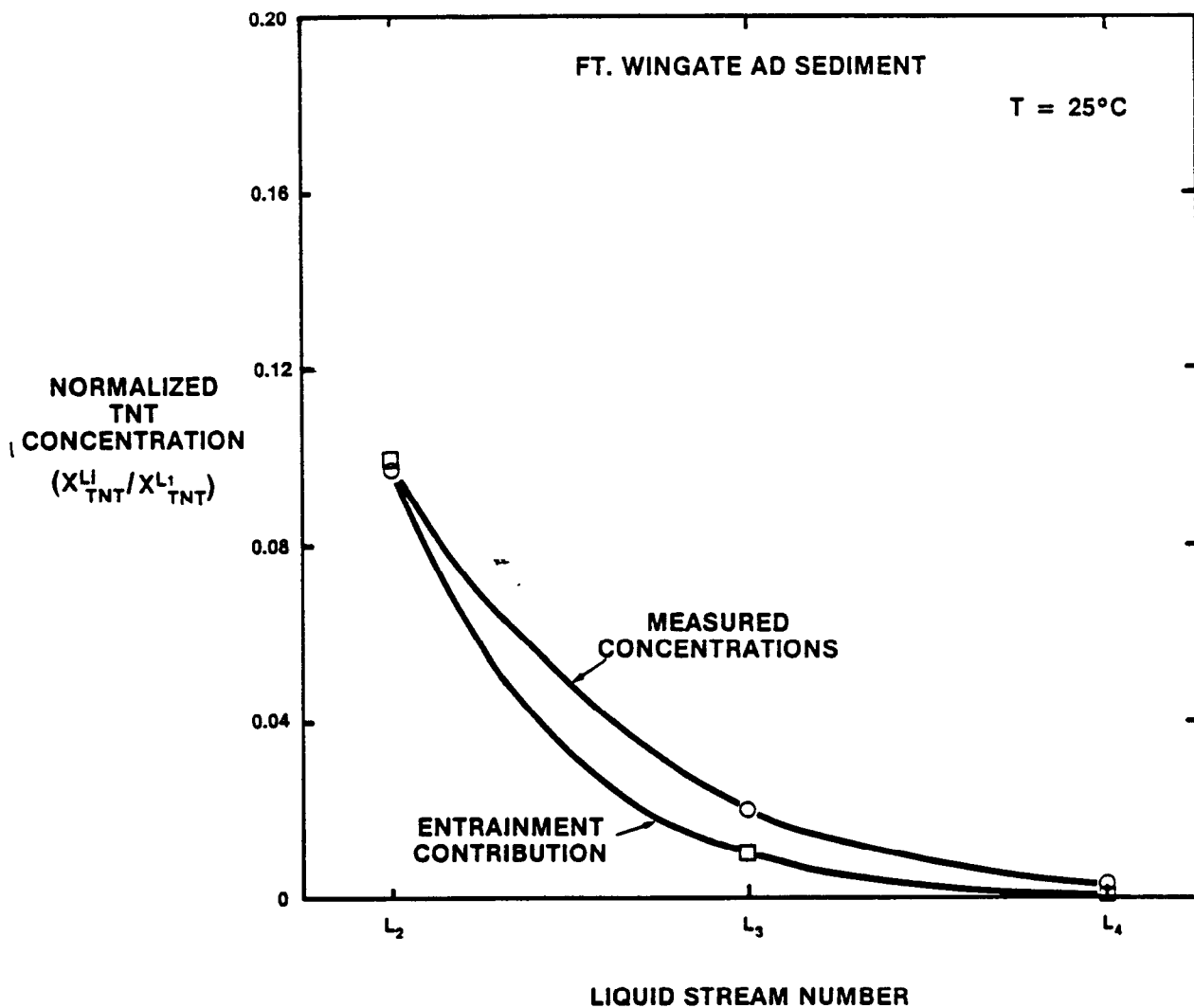


Figure 4-19
 FT. WINGATE AD ENTRAINMENT EFFECTS

USATHAMA

SOURCE: ESE, 1984.

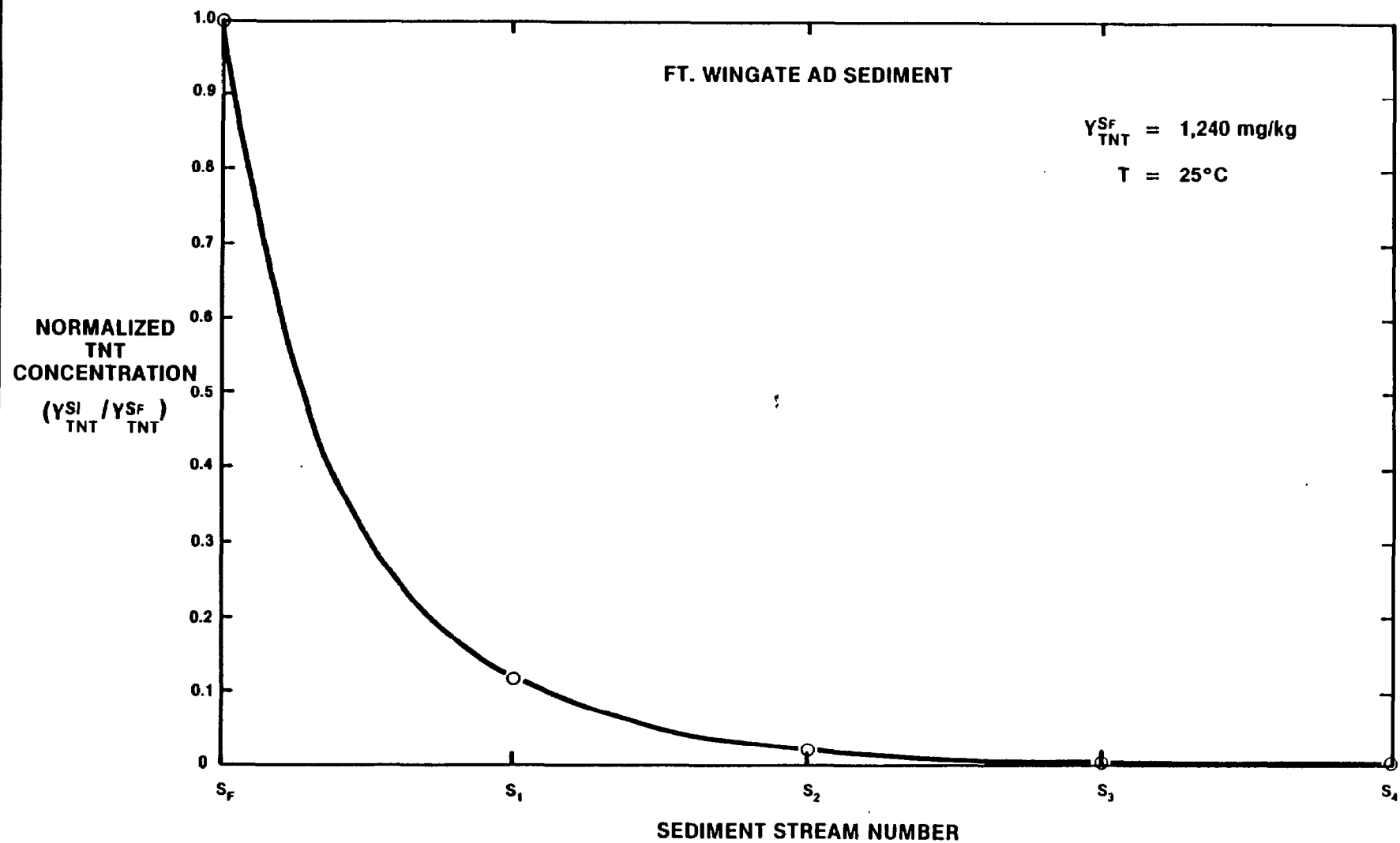


Figure 4-20
NORMALIZED SEDIMENT TNT CONCENTRATION IN
COUNTERCURRENT LEACHING --FT. WINGATE AD

SOURCE: ESE, 1984.

USATHAMA

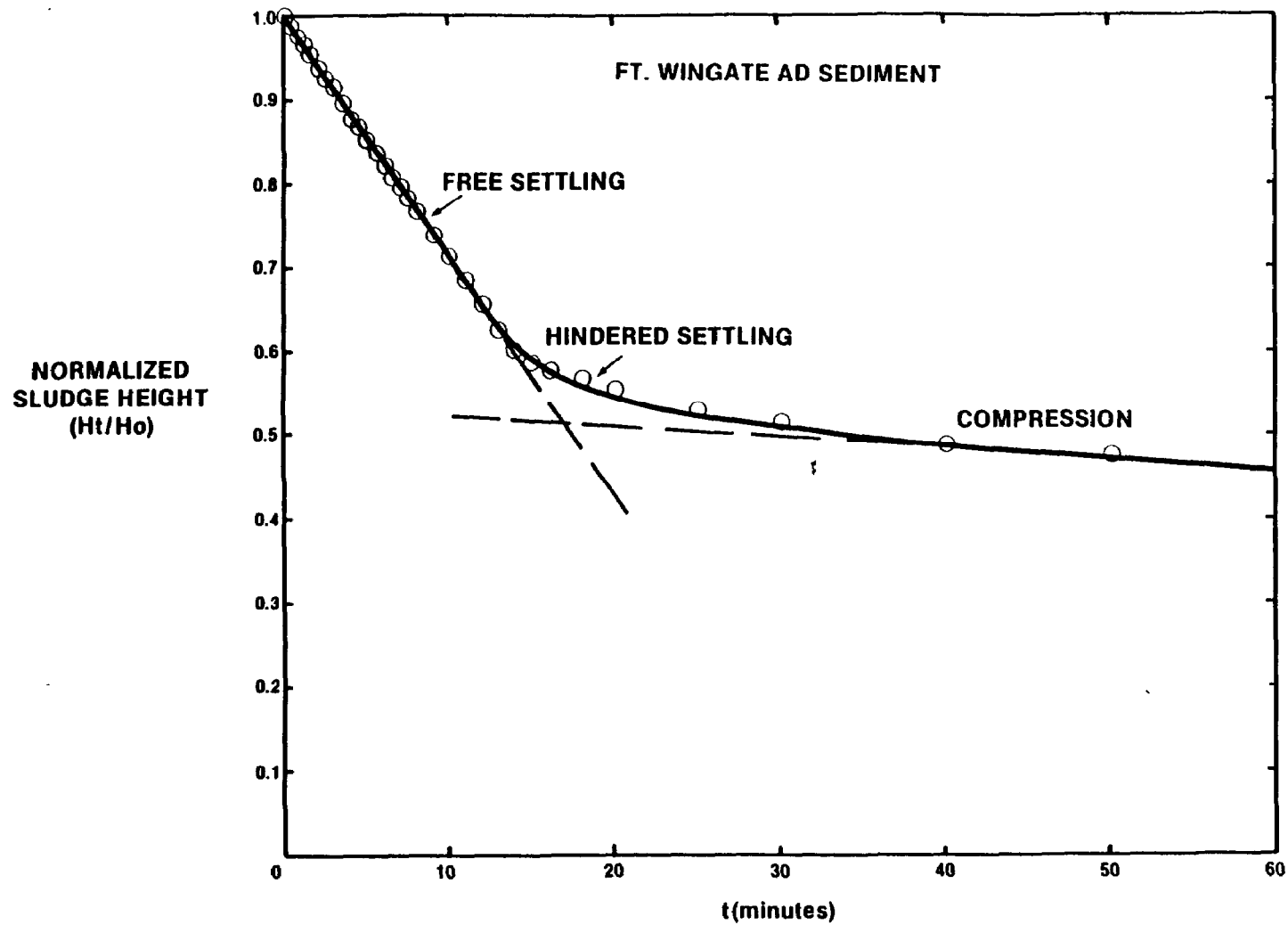


Figure 4-21
FT. WINGATE AD SETTLING TEST

USATHAMA

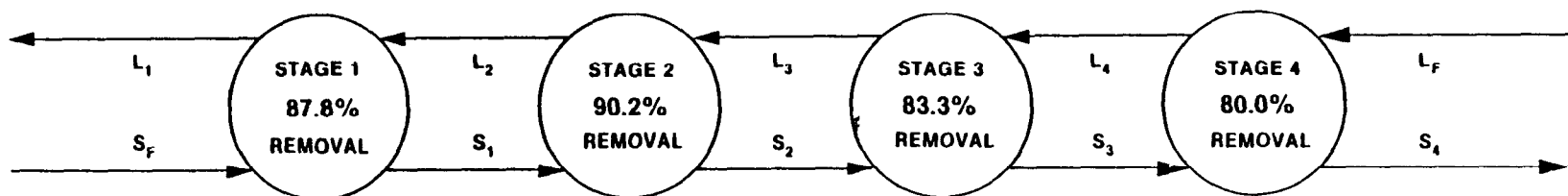
385 ml
90.9% ACETONE
5,500 mg/l TNT

385 ml
98.5% ACETONE
617 mg/l TNT

385 ml
99.4% ACETONE
55 mg/l TNT

385 ml
99.6% ACETONE
9.5 mg/l TNT

385 ml
100% ACETONE



140 GRAMS
25.0% MOISTURE
19,300 mg/kg TNT

128.3 GRAMS
21.9% MOISTURE
2,350 mg/kg TNT

123.8 GRAMS
21.0% MOISTURE
231 mg/kg TNT

127.1 GRAMS
25.9% MOISTURE
40.3 mg/kg TNT

120.2 GRAMS
18.8% MOISTURE
7.0 mg/kg TNT

OVERALL REMOVAL: 99.96%

*DATA
USED*

Figure 4-22
COUNTERCURRENT EXTRACTION SIMULATION--NAVAJO AD

SOURCE: ESE, 1984.

USATHAMA

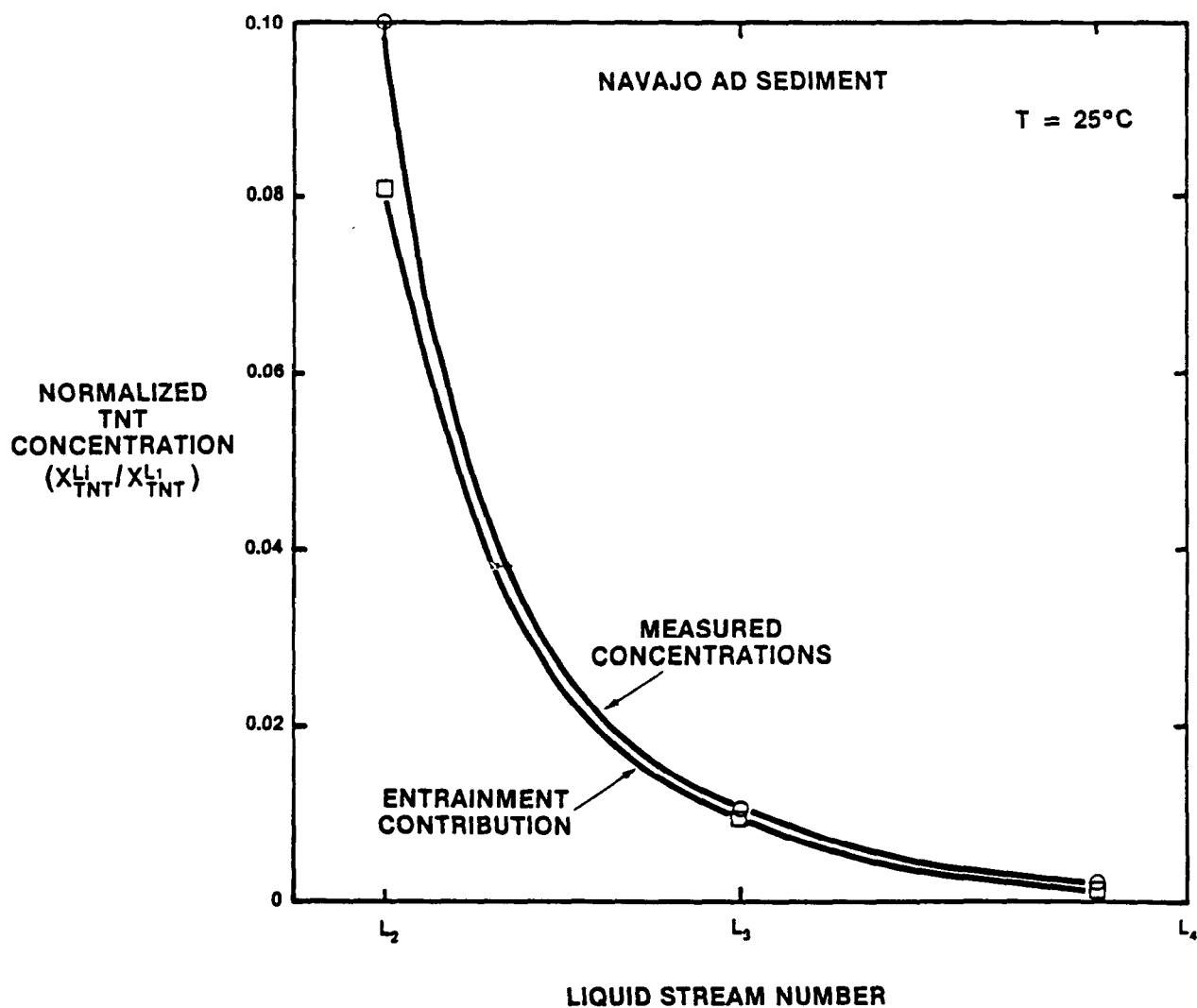


Figure 4-24
 NAVAJO AD ENTRAINMENT EFFECTS

SOURCE: ESE, 1984.

USATHAMA

4-39

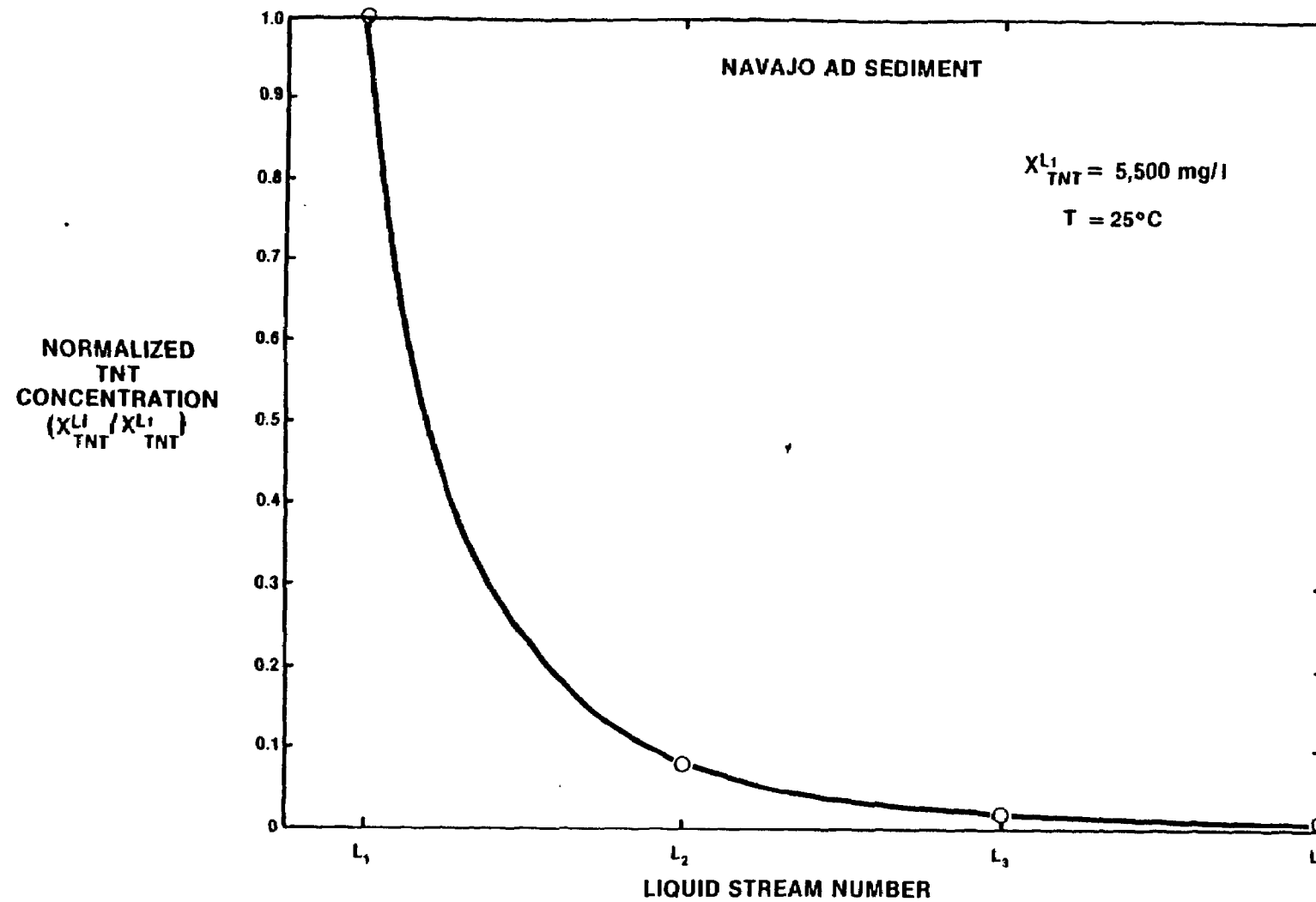


Figure 4-23
 NORMALIZED LIQUID TNT
 CONCENTRATION IN COUNTERCURRENT
 LEACHING--NAVAJO AD
 SOURCE: ESE, 1984.

USATHAMA

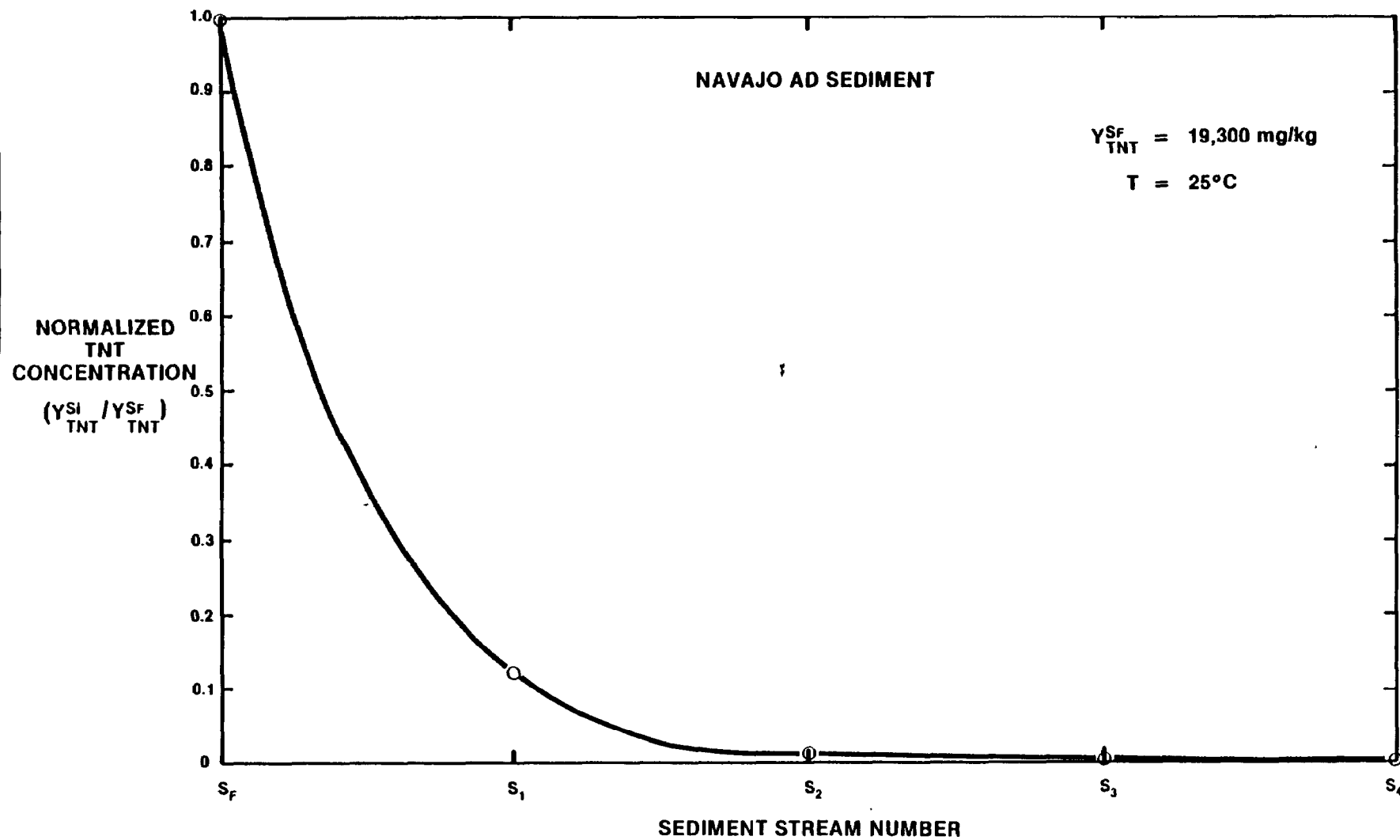


Figure 4-25
 NORMALIZED SEDIMENT TNT CONCENTRATION IN
 COUNTERCURRENT LEACHING --NAVAJO AD

USATHAMA

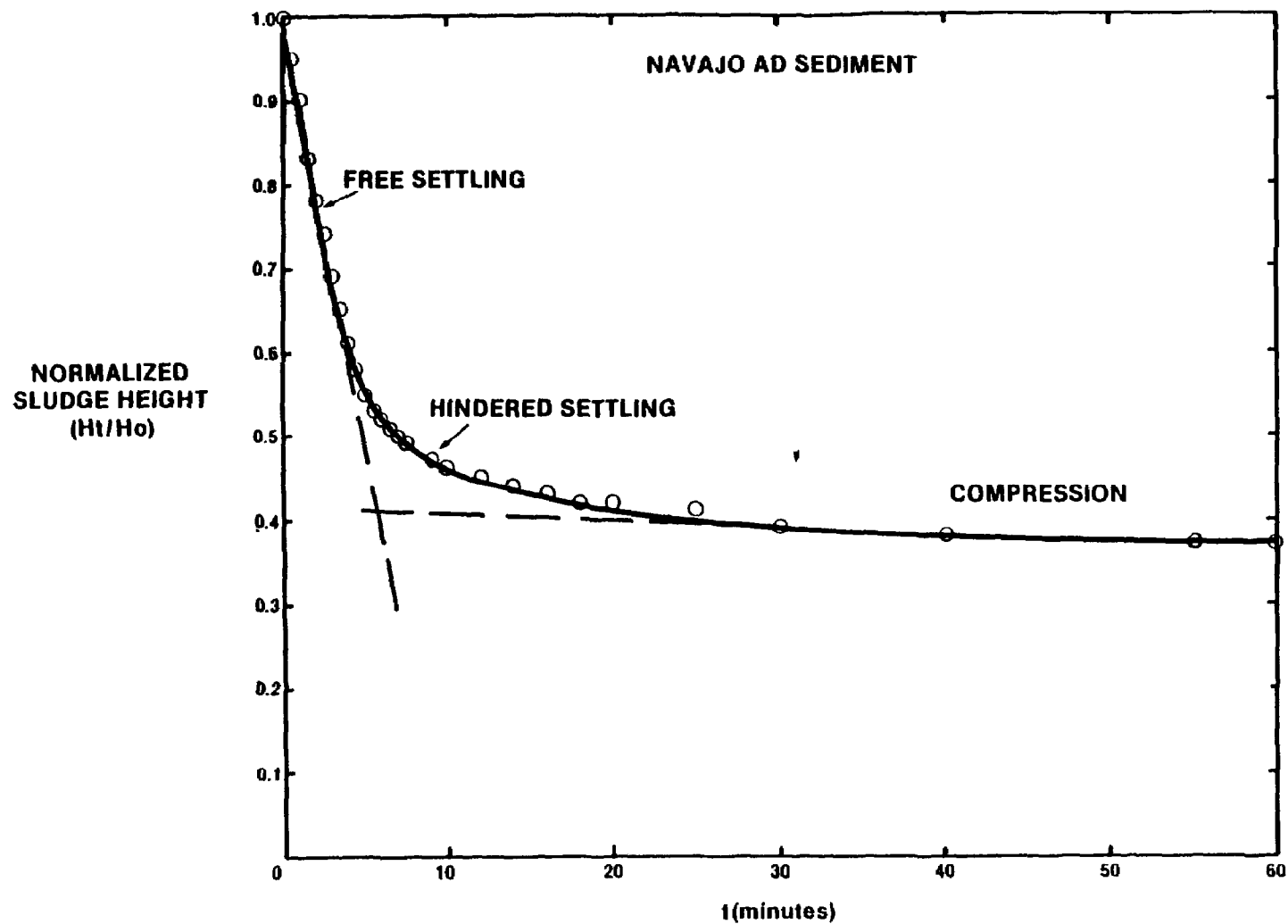


Figure 4-26
NAVAJO AD SETTLING TEST

USATHAMA

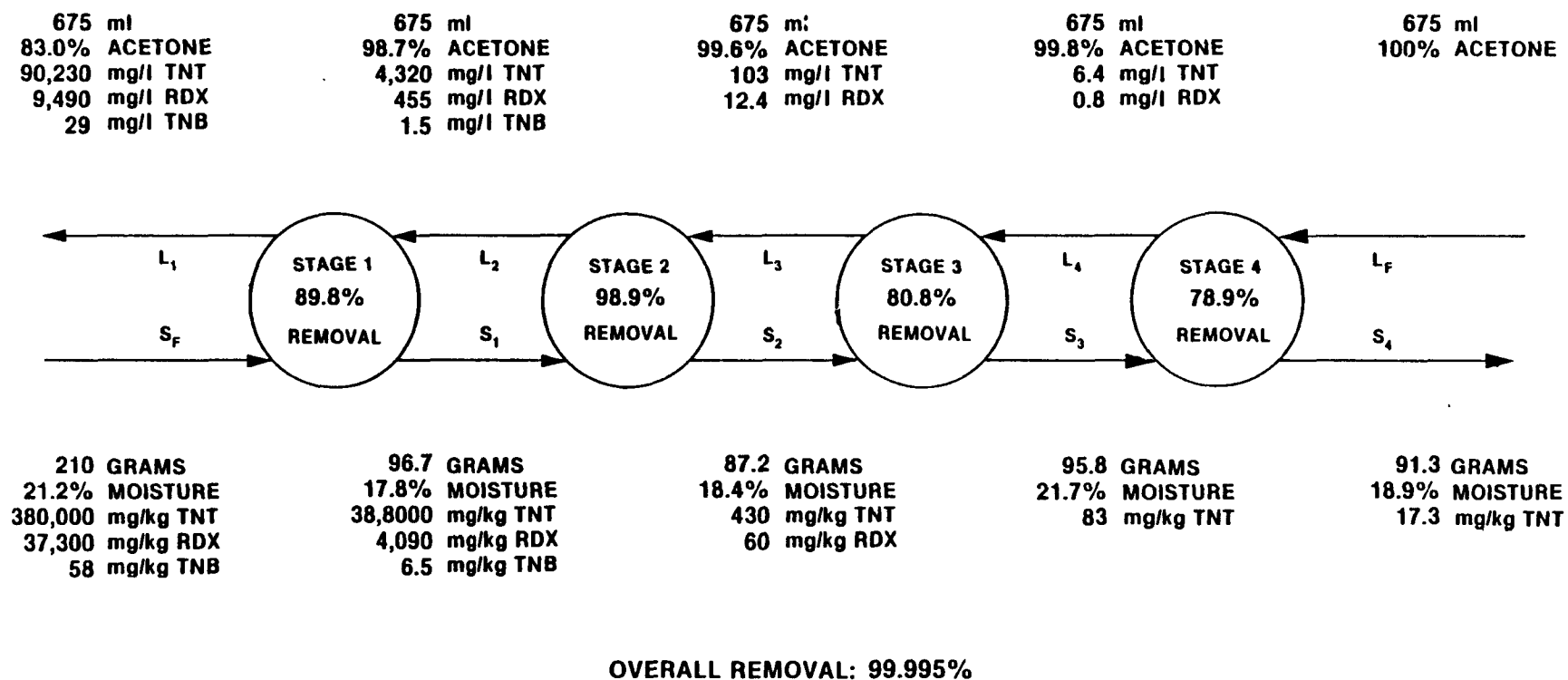


Figure 4-27
COUNTERCURRENT EXTRACTION SIMULATION --LOUISIANA AAP

SOURCE: ESE, 1984.

USATHAMA

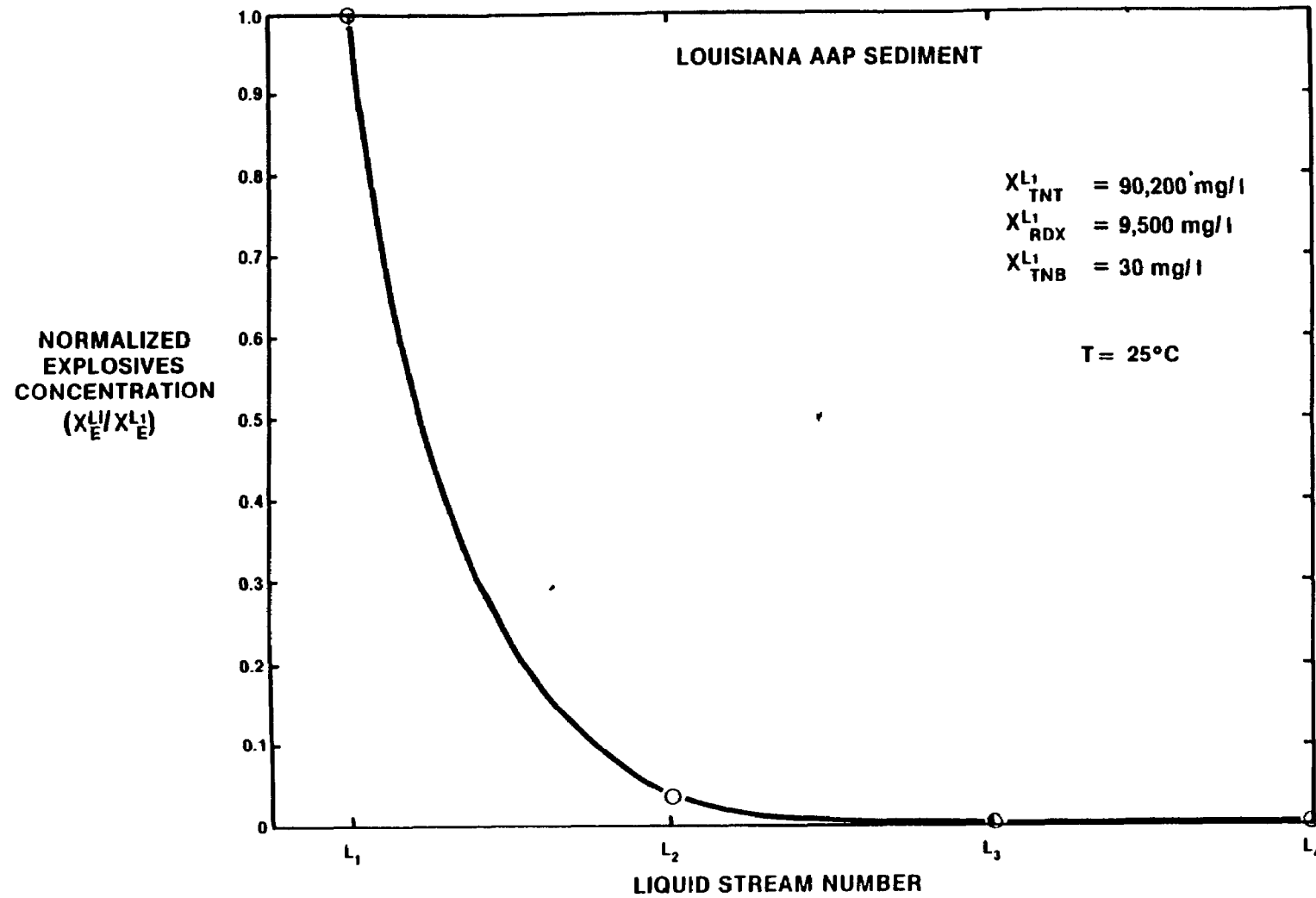


Figure 4-28
 NORMALIZED LIQUID EXPLOSIVES
 CONCENTRATION IN COUNTERCURRENT
 LEACHING--LOUISIANA AAP

SOURCE: ESE 4884

USATHAMA

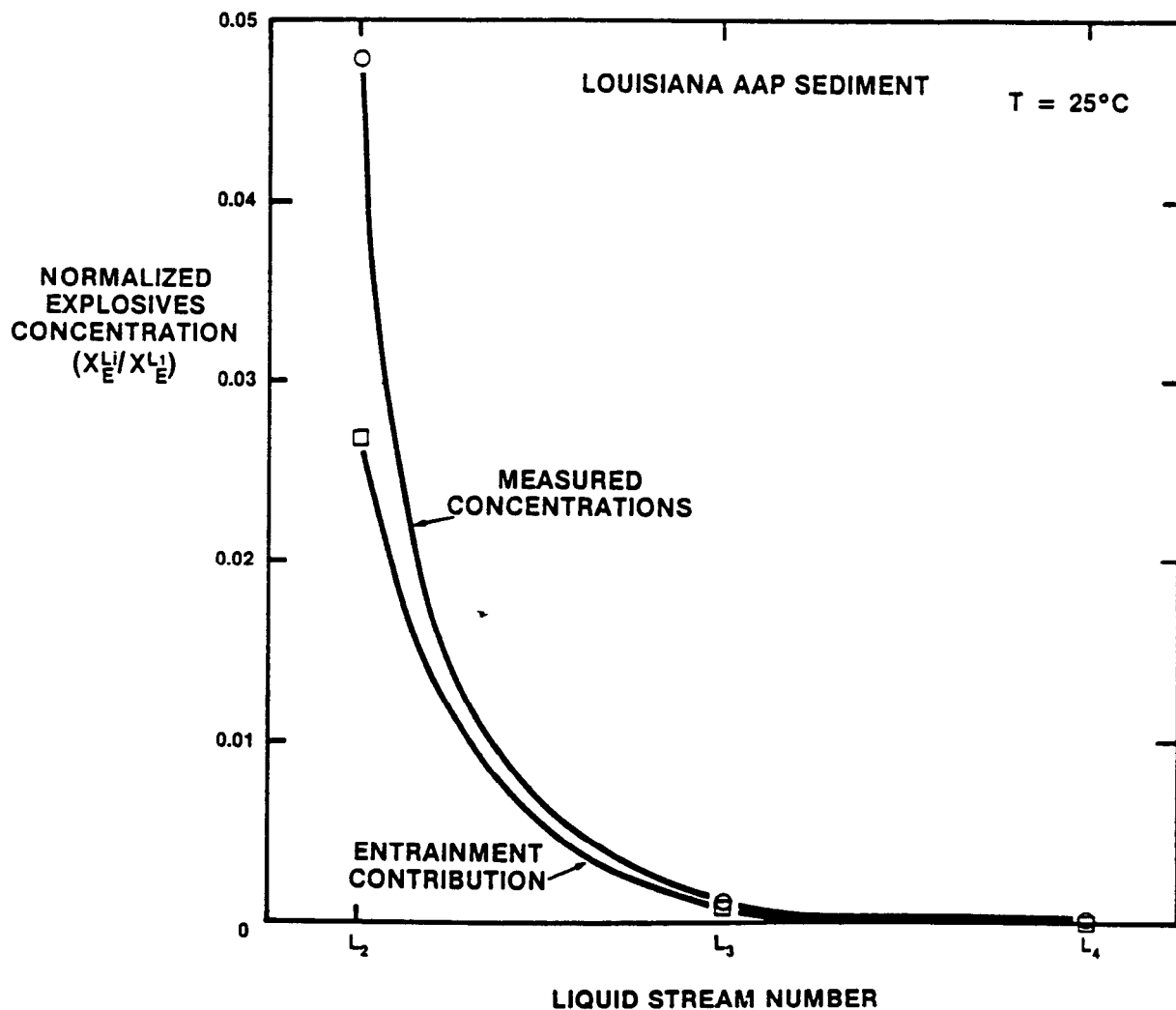


Figure 4-29
LOUISIANA AAP ENTRAINMENT EFFECTS

USATHAMA

SOURCE: ESE, 1984.

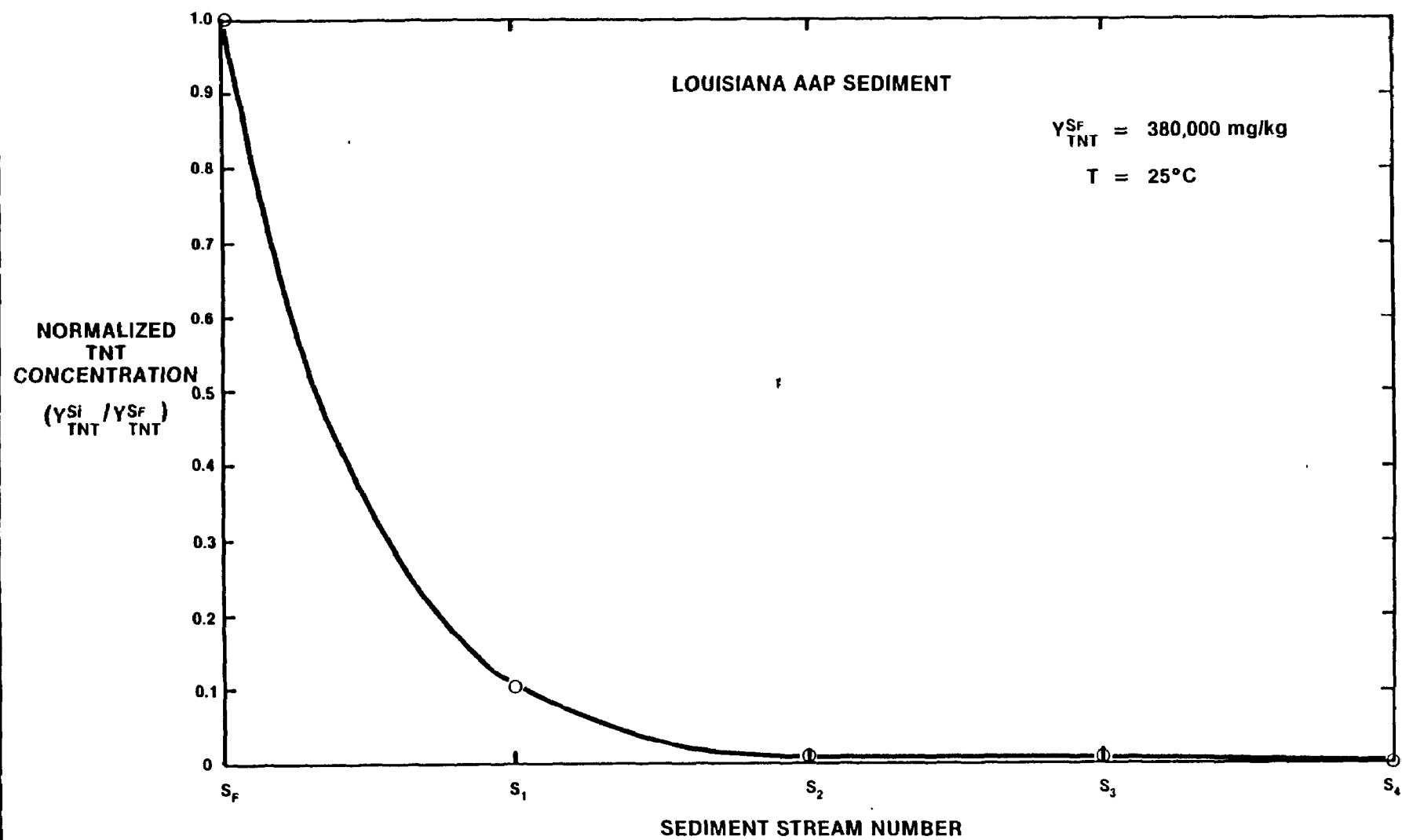


Figure 4-30
NORMALIZED SEDIMENT TNT CONCENTRATION IN
COUNTERCURRENT LEACHING--LOUISIANA AAP

5.0 SUMMARY AND CONCLUSIONS

The laboratory study indicated that wet, explosives-laden sediment can be effectively decontaminated by leaching with acetone. Three contact stages reduced the explosives concentration in Ft. Wingate AD sediment to less than 10 mg/kg. Four contact stages were required to reduce the explosives concentration in the Navajo AD sediment to less than 10 mg/kg. The explosives concentration in the Louisiana AAP sediment was 17 mg/kg after four contact stages. It is apparent that a fifth contact stage with greater than 50-percent efficiency would reduce the explosives content to less than 10 mg/kg.

The initial sediment explosives concentration, the final sediment explosives concentration, and the calculated 4-stage removal efficiencies are shown in Table 5-1 for all three sediments. The Louisiana AAP sediment, which was initially the most contaminated, contained the highest final concentration of explosives after four contact stages, but experienced the highest removal efficiency. The Ft. Wingate AD sediment was initially the least contaminated, and the final residue had the lowest concentration of explosives. The Ft. Wingate AD sediment had the lowest overall removal. The Navajo AD sediment had intermediate initial contamination and had intermediate final concentration and removal.

Table 5-1. Initial Sediment Explosives Concentration, Final Sediment Explosives Concentration, and Calculated 4-Stage Removal Efficiencies

| Sediment | Initial Explosives Concentration (mg/kg) | Final Explosives Concentration (mg/kg) | 4-Stage Removal Efficiency (%) |
|----------------|---|---|---|
| Ft. Wingate AD | 1,200 | 6.0 | 99.5 |
| Navajo AD | 19,000 | 7.0 | 99.96 |
| Louisiana AAP | 420,000 | 17.0 | 99.996 |

Source: ESE, 1984.

The individual stage removal efficiencies for all three countercurrent extraction simulations are plotted in Figure 5-1 against the natural logarithm (ln) of TNT concentration of the sediment entering the stage. Stage efficiencies are limited to about 90 percent (neglecting the outlying Louisiana AAP point at 99 percent) by entrainment. The lower-stage efficiencies at low TNT concentration indicate adsorption equilibrium limitations.

The different stage requirements necessary to achieve a given degree of removal or final residue concentration level indicate that a treatment system based on solvent extraction should have a variable number of contact stages available. Continuous countercurrent contact devices can be constructed such that by varying operational parameters such as residence time, feed-to-solvent ratio, and degree of mixing, the number of effective stages can be varied.

The individual solubilities of TNT, DNT, RDX, and tetryl and their mixed component solubilities in acetone/water were found to vary nonlinearly with acetone fraction in the solvent. In all cases the solubilities are low in acetone/water mixtures of less than 50-percent acetone. The solubilities increase continuously from 50-percent acetone to their maximum at 100-percent acetone in the solvent.

At 25°C, saturated solutions of TNT and of DNT in acetone/water mixtures of between approximately 50-percent acetone and 90-percent acetone form two liquid phases in equilibrium with solid solute. The less dense, top phase consists of approximately equal proportions of acetone and water with 4- or 5-percent solute. The denser bottom phase consists of approximately equal proportions of solute and acetone with 5-percent water.

The solubility results should be used to select the feed-to-solvent ratio for the solvent extraction treatment system. Both the amount of water

and the concentration of explosives should be considered. The total amount of solvent should be in excess of that needed to solubilize all of the explosives at the acetone/water ratio established.

The region of liquid-liquid 2-phase behavior should be avoided in the leaching operation. Liquid-liquid interfacial tension could hinder penetration of solvent through the sediment.

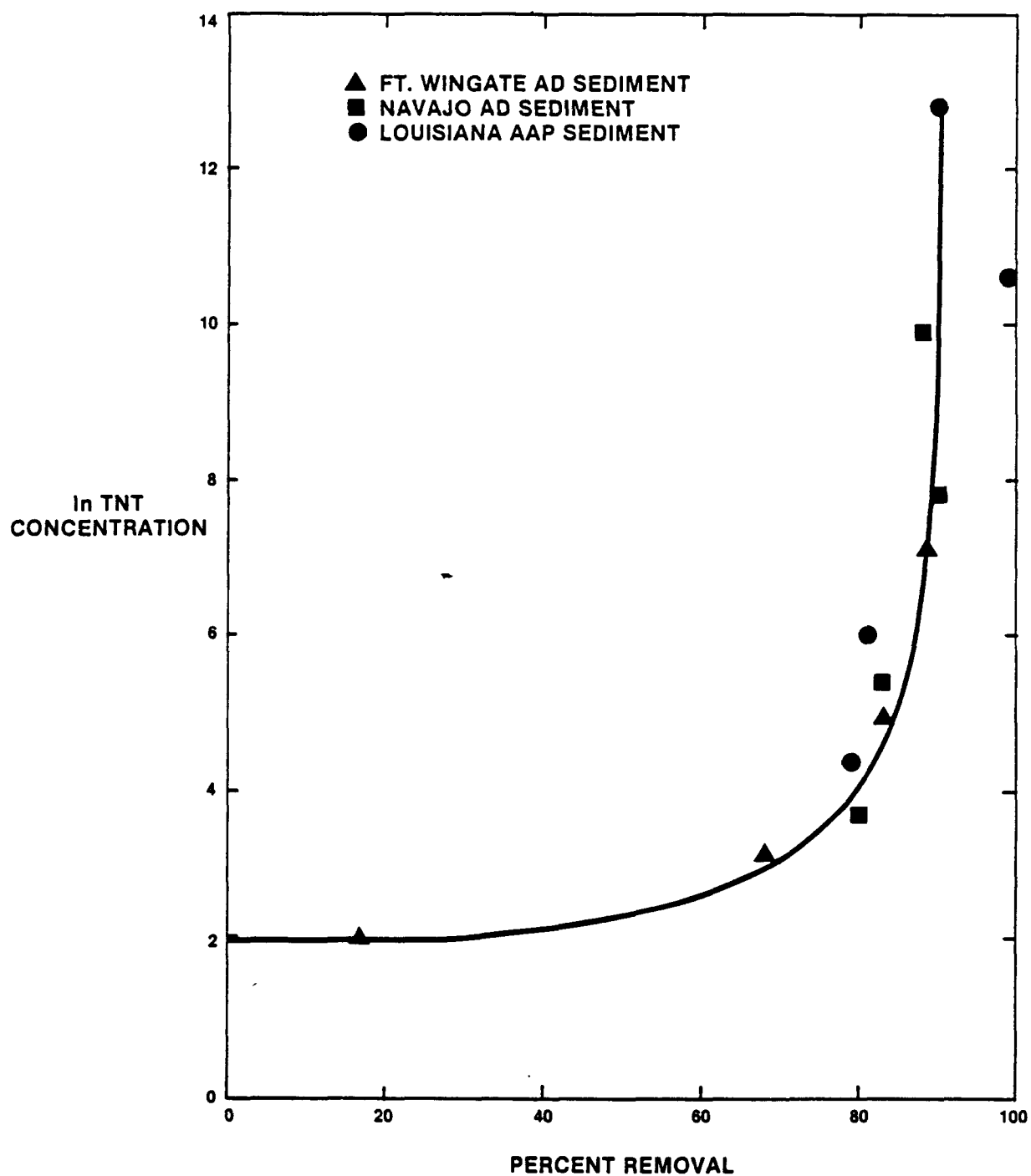


Figure 5-1
STAGEWISE TNT REMOVALS VERSUS
ENTERING TNT CONCENTRATIONS

SOURCE: ESE, 1984.

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6.0 CONCEPTUAL TREATMENT SYSTEM DESIGN

A conceptual design for the solvent extraction treatment system was developed to provide information for USATHAMA to estimate capital and operating costs. Cost estimates are being prepared in conjunction with Engineering-Science and will be published in "Cost Analysis Methodology Development for Installation Restoration Development."

Figure 6-1 is the process flow diagram for the solvent extraction system. The sediment is milled under water to reduce the particle size. The wet milled sediment (50 percent moisture) is then screw conveyed to the extractor. The screw conveyor is sloped toward the mill and will dewater the sediment to approximately 30 percent water. Feed sediments with greater than 30 percent water will generate excess water at the mill. Sediments with less than 30 percent water will require make-up water to the mill (shown as negative flow on material balance). Make-up water will be recycled from the solvent recovery still. Excess water and standing water in the lagoon will be treated by granular activated carbon.

In the extractor, sediments are screw conveyed upward and mixed with acetone which flows countercurrent to the sediment. Clean, acetone-wet solids enter the dryer where they are heated by indirect contact with hot oil. The solids are conveyed through the continuous dryer and exit as clean, dry solids, suitable for landfilling in a cleared empty lagoon at the site. Vapors from the dryer go to the overhead condenser of the solvent recovery column.

The explosives-laden solvent (extract) overflows the hopper on the extractor to an extract tank where entrained solids settle. The extract is filtered and then preheated in a feed/distillate heat exchanger. In the solvent recovery column the extract is split into three streams. The overhead stream is the recovered solvent which is 97 percent acetone and

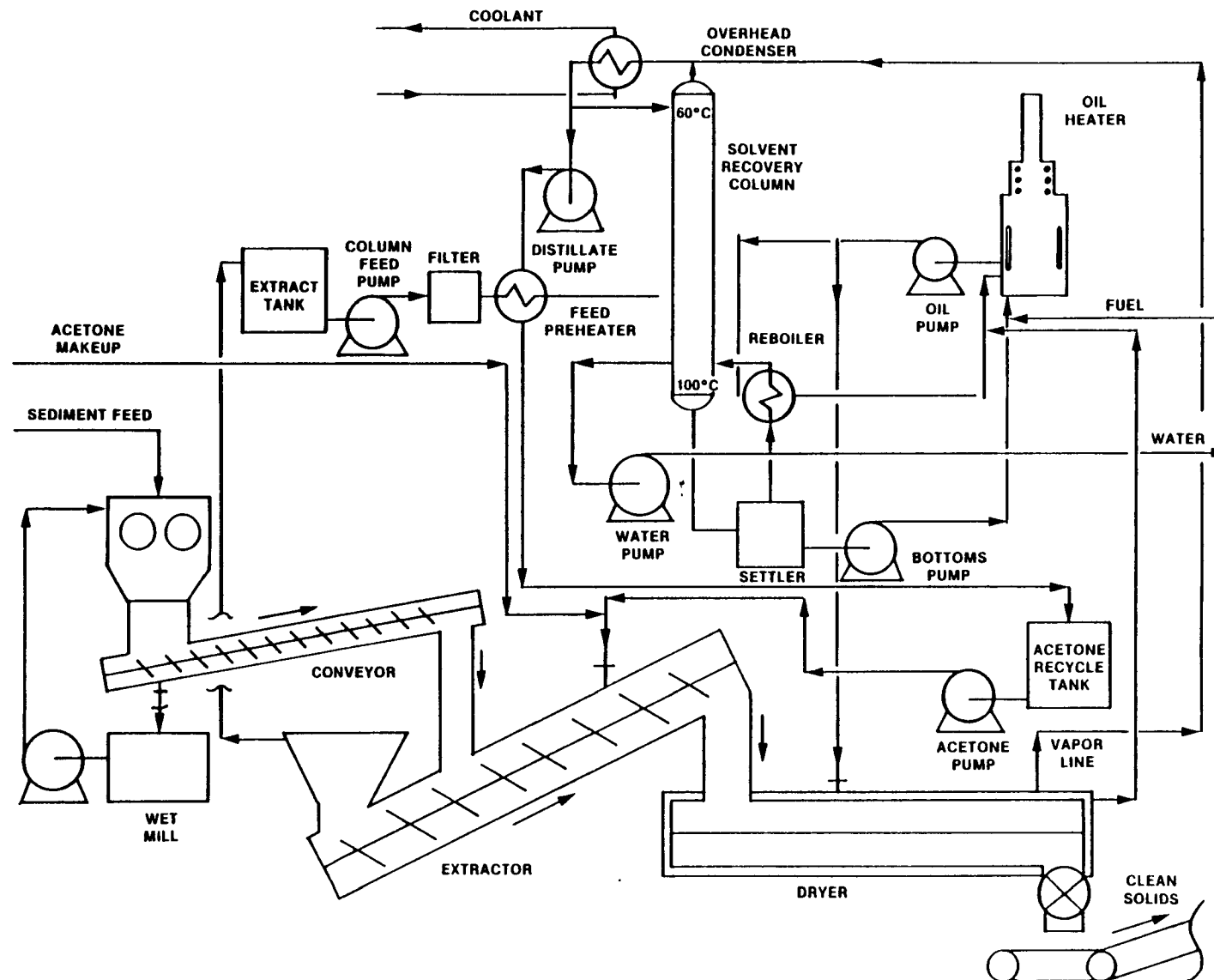


Figure 6-1
SOLVENT EXTRACTION SYSTEM
PROCESS FLOW DIAGRAM

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3 percent water. The column bottoms go to an insulated settler where molten explosives phase-separate from the water.

The molten explosives will be burned in the hot oil heater to provide heat for the process. It may be necessary to blend the explosives with fuel oil or acetone for safety purposes prior to burning. With heavily contaminated sediments the explosives can provide a significant portion of process heat requirements.

The water from the settler is heated in the reboiler and returned to the column. Water is removed from the column as a liquid side-stream at 100°C. The explosives concentration in the water is expected to be less than 0.001 mg/l. The acetone content will be less than 100 mg/l. If 100 mg/l acetone is too high for direct discharge or treatment in an existing treatment facility, an auxiliary distillation column can be used to reduce the acetone concentration further.

All equipment that contains acetone will be maintained at slight positive pressure (several inches of water column) with nitrogen for fire prevention.

Material balances were generated for decontamination of pink-water lagoons at Cornhusker AAP, Savannah AD Activity, and Louisiana AAP. The material balances are based on cleanup of Cornhusker AAP lagoons in 1 year, Savannah AD Activity lagoons in 2 years, and Louisiana AAP lagoons in 5 years. The material balances for Cornhusker AAP, Savannah AD Activity, and Louisiana AAP are presented in Tables 6-1, 6-2, and 6-3, respectively. The stream numbers in the tables correspond to the stream numbers on the block diagram (Figure 6-2).

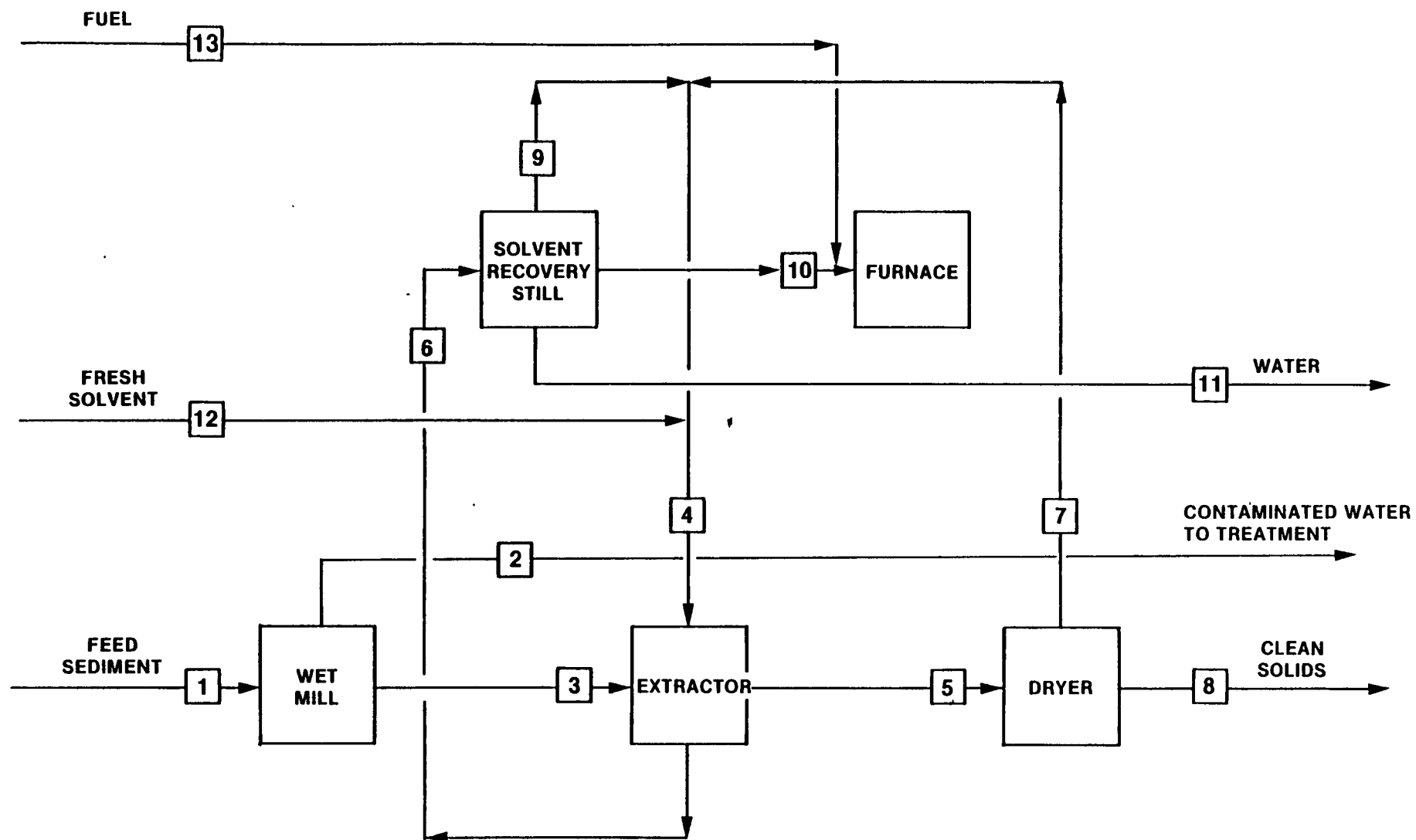


Figure 6-2
SOLVENT EXTRACTION SYSTEM BLOCK DIAGRAM

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Table 6-1. Cornhusker AAP Solvent Extraction Material Balance

| Stream Number | Explosive (lb/hr) | Inerts (lb/hr) | Water (lb/hr) | Acetone (lb/hr) | Total (lb/hr) |
|---------------|-------------------|----------------|---------------|-----------------|-----------------|
| 1 | 41 | 4,107 | 1,102 | -- | 5,250 |
| 2 | -- | -- | -631 | -- | -631 [1.26] |
| 3 | 41 | 4,107 | 1,733 | -- | 5,881 |
| 4 | -- | -- | 83 | 2,694 | 2,777 |
| 5 | -- | 4,107 | 31 | 995 | 5,133 |
| 6 | 41 | -- | 1,785 | 1,699 | 3,525 [7.83] |
| 7 | -- | -- | 31 | 995 | 1,026 |
| 8 | <10 mg/kg | 4,107 | -- | -- | 4,107 |
| 9 | -- | -- | 52 | 1,699 | 1,751 [4.42] |
| 10 | 41 | — | — | — | 41 [0.05] |
| 11 | <1 µg/l | -- | 1,102 | <100 mg/l | 1,102 [2.2] |
| 12 | -- | -- | -- | 15 | 15 |

[] = gallons/minute.

Table 6-2. Louisiana AAP Solvent Extraction Material Balance

| Stream Number | Explosive (lb/hr) | Inerts (lb/hr) | Water (lb/hr) | Acetone (lb/hr) | Total (lb/hr) |
|---------------|-------------------|----------------|---------------|-----------------|------------------|
| 1 | 890 | 3,562 | 4,452 | -- | 8,904 |
| 2 | -- | -- | 2,544 | -- | 2,544 [5.08] |
| 3 | 890 | 3,562 | 1,908 | -- | 6,360 |
| 4 | -- | -- | 177 | 5,722 | 5,899 |
| 5 | 0.03 <10 ppm | 3,562 | 27 | 864 | 4,453 |
| 6 | 890 | -- | 2,058 | 4,858 | 7,806 [18.13] |
| 7 | -- | -- | 27 | 864 | 891 |
| 8 | 0.03 | 3,562 | -- | -- | 3,562 |
| 9 | -- | -- | 150 | 4,858 | 5,008 [12.7] |
| 10 | 890 | -- | -- | -- | 890 [1.2] |
| 11 | <1 µg/l | -- | 1,908 | <100 mg/l | 1,908 [3.8] |
| 12 | -- | -- | -- | 30 | 30 |

[] = gallons/minute.

Table 6-3. Savannah AD Activity Solvent Extraction Material Balance

| Stream Number | Explosive (lb/hr) | Inerts (lb/hr) | Water (lb/hr) | Acetone (lb/hr) | Total (lb/hr) |
|---------------|-------------------|----------------|---------------|-----------------|-------------------------|
| 1 | 111 | 2,112 | 556/2,223* | -- | 2,779/4,446* |
| 2 | -- | -- | -397/1,270* | -- | -397/1,270 [0.8/2.5] |
| 3 | 111 | 2,112 | 953 | -- | 3,176 |
| 4 | -- | -- | 60 | 1,940 | 2,000 |
| 5 | -- | 2,112 | 16 | 512 | 2,640 |
| 6 | 111 | -- | 997 | 1,428 | 2,536 [5.7] |
| 7 | -- | -- | 16 | 512 | 528 |
| 8 | <10 mg/kg | 2,112 | -- | -- | 2,112 |
| 9 | -- | -- | 44 | 1,428 | 1,472 [3.7] |
| 10 | 111 | -- | -- | -- | 111 [0.15] |
| 11 | <1 µg/l | -- | 556/953* | <100 mg/l | 556/953* [1.1/1.9] |
| 12 | -- | -- | -- | 10 | 10 |

* = (upper lagoon/lower lagoon)

[] = gallons/minute.

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APPENDIX A
ANALYTICAL METHODS

APPENDIX A
ANALYTICAL METHODS

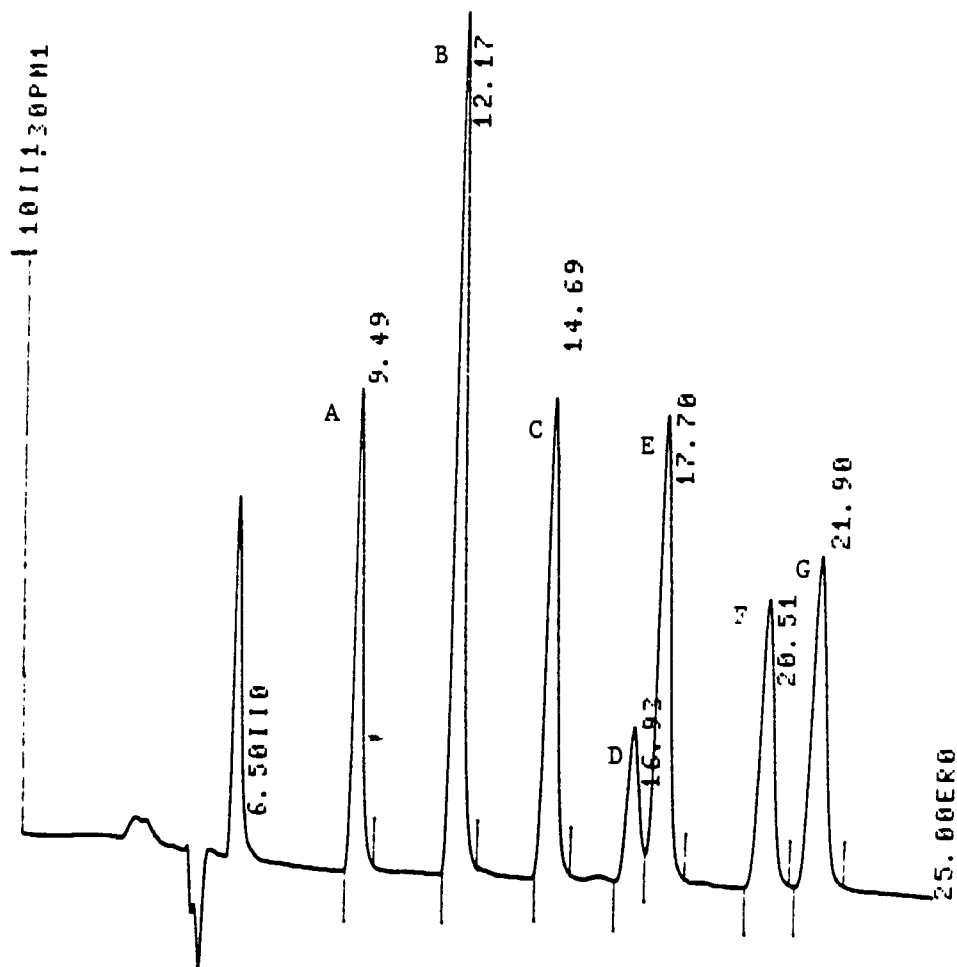
ANALYSIS OF EXPLOSIVES IN SEDIMENT BY HPLC/UV

Weigh 20 gm of sediment into a 50-ml centrifuge tube. Add 5 gm of anhydrous sodium sulfate to the tube and mix (more anhydrous sodium sulfate may be necessary if the sample has a high moisture content). Extract the sample by shaking sequentially with four 35-ml portions of acetone using a shaking time of 2 minutes. After each extraction, centrifuge the sample and decant the extract through an anhydrous sodium sulfate bed into a Kuderna-Danish (K-D) concentration apparatus equipped with a 25-ml receiver. Concentrate the extract and solvent exchange to 2 ml of acetonitrile. Dilute the extract to 5 ml with water. Analyze the extract by HPLC with ultraviolet absorption detection at 230 nm. In all cases, 5-micron (25 cm x 4.6 mm ID) Ultrasphere ODS columns were used. A flow rate of 1 ml/minute and an injection volume of 250 ul were standard. A representative chromatogram and the chromatographic conditions are shown in Figure A-1.

ANALYSIS OF LIQUID PHASES BY HPLC/UV

The liquid phases from the solubility tests were diluted into water-methanol mixtures prior to analysis. Those phases which contained high levels of explosives were diluted first into acetone and further diluted into water-methanol to avoid exceeding the solubility. For the individual explosives solubility tests, the amount of methanol in the mobile phase was adjusted to provide a retention time of 6 to 10 minutes for the explosives. A 45-percent methanol in water isocratic mobile phase was used for analysis of the liquid phase in the mixed explosives solubility tests.

HPLC conditions for both the liquid and solid samples from the leach rate and countercurrent tests are given in Figure A-1.



CONDITIONS:

250- μ l injection volume
 Isocratic elution: 50-percent methanol/
 50-percent water
 Flow rate: 1 ml/minute
 Columns: Two 25-cm x 4.6-mm ID Ultrasphere ODS
 5-micron columns in series
 Ultraviolet detection at 230 nanometers

KEY:

A. RDX
 B. TNB
 C. Tetryl
 D. Nitrobenzene
 E. TNT
 F. 2,6-DNT
 G. 2,4-DNT

Figure A-1
HPLC/UV CHROMATOGRAM OF
EXPLOSIVES FOR STANDARD SEDIMENT
METHOD DOCUMENTATION
 SOURCE: ESE, 1984.

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METHOD PRECISION AND ACCURACY

Spiking experiments were performed to generate precision and accuracy data for the analysis of explosives in sediment. Explosives were spiked into clean soil at several levels in the 0.2- to 20-ug/gm range. Replicate analyses were performed using the procedure outlined in Section 3.1. Table A-1 lists the spike levels, precision, and accuracy data obtained from these experiments. The method was not applicable to tetryl because it decomposed in hot acetone during the K-D concentration step.

GC/TCD ANALYSIS FOR WATER AND ACETONE CONTENT

Gas chromatography with a thermal conductivity detector (GC/TCD) was used to analyze the liquid phases from the solubility, leach rate, and countercurrent extraction tests for acetone and water content. The chromatographic conditions and a representative chromatogram are shown in Figure A-2.

LIQUID CONTENT OF SEDIMENTS

The sediments from the leach rate and countercurrent extraction tests were analyzed for liquid using a procedure similar to ASTM Method D2216-71. An aliquot of sediment (at least 15 gm) was weighed and placed in a convection oven at 105°C for at least 12 hours. The dried sediment was then reweighed to determine the liquid content. The liquid measured by this method included both water and acetone. The percent moisture (or percent water plus acetone) was calculated by dividing the weight of the moisture by the initial weight of the undried sediment.

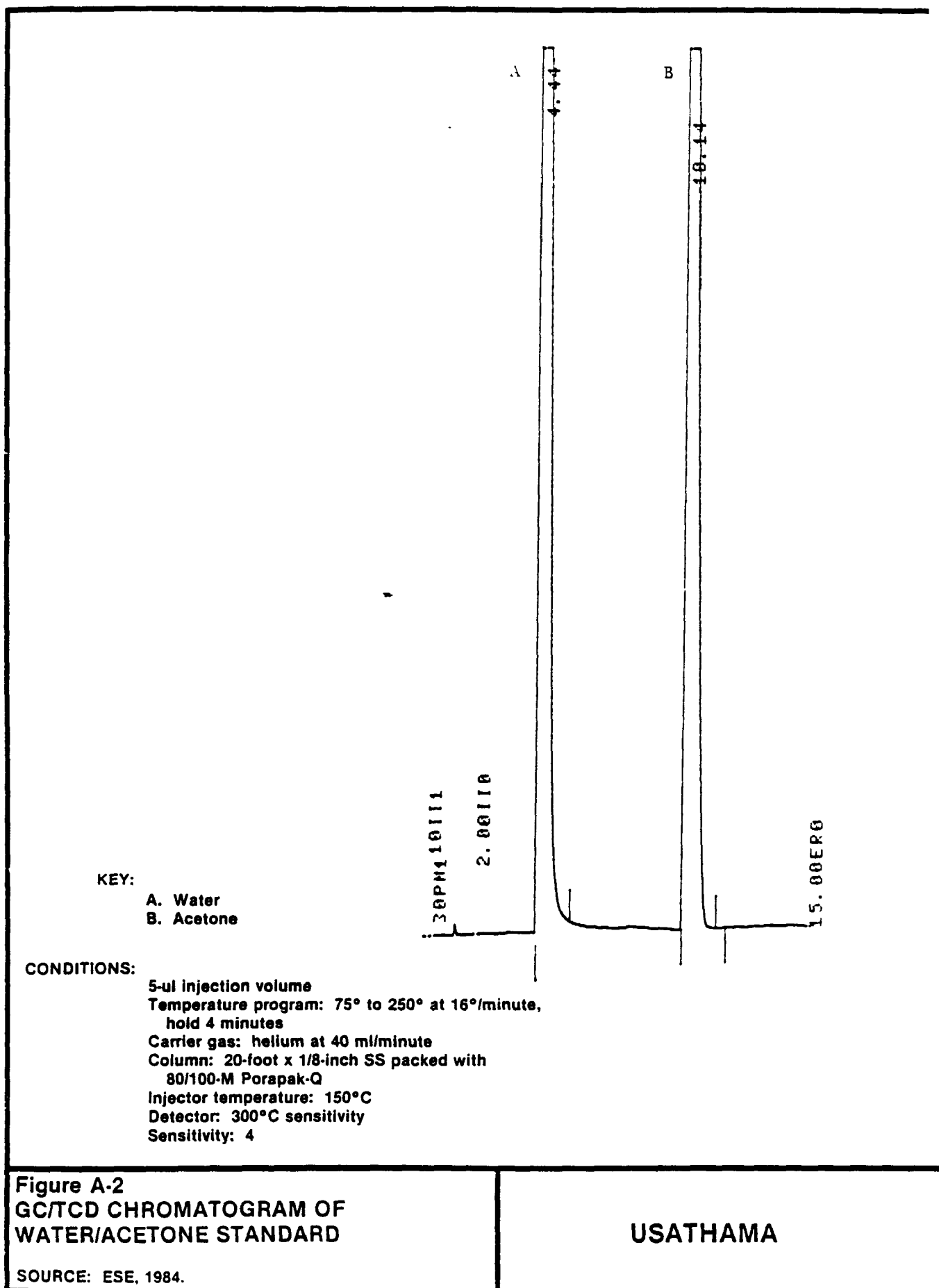


Table A-1. Explosives in Sediment Method--Precision and Accuracy Data

| Spike Level (ug/g) | Found Levels (ug/g) | Average Found Level (ug/g) | Percent RSD | Average Percent Recovery |
|-----------------------|------------------------|-------------------------------|-------------|--------------------------|
| <u>RDX</u> | | | | |
| 0.267 | 0.262, 0.266, 0.255 | 0.261 | 2.1 | 97.8 |
| 0.534 | 0.581, 0.571, 0.589 | 0.580 | 1.6 | 108.7 |
| 1.34 | 1.10, 1.06, 1.06 | 1.07 | 2.2 | 80.1 |
| 26.7 | 26.8, 27.1, 27.1 | 27.0 | 0.6 | 101.1 |
| | Overall | | 1.6 | 96.9 |
| <u>TNT</u> | | | | |
| 0.204 | 0.146, 0.170, 0.196 | 0.171 | 14.6 | 83.7 |
| 0.408 | 0.270, 0.495, 0.563 | 0.443 | 34.6 | 108.5 |
| 1.02 | 0.631, 0.699, 0.596 | 0.642 | 8.2 | 62.9 |
| 20.4 | 13.7, 16.0, 14.8 | 14.8 | 7.8 | 72.7 |
| | Overall | | 16.3 | 82.0 |
| <u>TNB</u> | | | | |
| 0.205 | 0.186, 0.153, 0.160 | 0.166 | 10.5 | 81.1 |
| 0.410 | 0.338, 0.359, 0.365 | 0.354 | 4.0 | 86.3 |
| 1.02 | 0.717, 0.703, 0.711 | 0.710 | 1.0 | 69.6 |
| 20.5 | 16.7, 17.0, 19.7 | 17.8 | 9.3 | 86.8 |
| | Overall | | 6.2 | 81.0 |
| <u>DNT</u> | | | | |
| 0.210 | 0.170, 0.170, 0.197 | 0.179 | 8.7 | 85.2 |
| 0.419 | 0.394, 0.386, 0.447 | 0.409 | 8.1 | 97.6 |
| 1.05 | 0.639, 0.577, 0.457 | 0.558 | 16.6 | 53.1 |
| 21.0 | 16.2, 19.7, 19.7 | 18.5 | 10.9 | 88.3 |
| | Overall | | 11.1 | 81.1 |

Source: ESE, 1984.

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